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- 19. GLANDS OF INTERNAL SECRETION, 12 illus-
- 20. REPRODUCTION AND EARLY DEVELOP-
- 21. BODY DEFENSE AGAINST DISEASE, 30 illus-
- 22. HEALTHFUL LIVING, 48 illustrations.
- FOODS AND DIET, 21 illustrations BACTERIA AND PARASITES, 26 illustrations. 24.
- MAJOR MALADIES, 26 illustrations.
- COMMUNITY HEALTH, 35 illustrations. 27. DRUGS AND MEDICINES, 29 illustrations
- 28. ALCOHOL AND TOBACCO, 24 illustrations.
- LIVING SAFELY, 47 illustrations.
- 30. FIRST AID, 37 illustrations.

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Volume XVI

NEW BOOKS_

September, 1953

No. 3

CONTENTS

CONTENTS
IN FUTURE NUMBERS
PUTTING THE "BUGS" TO WORK Joseph Bonnano
CHELATING AGENTS
Harold Narcus
WRITING A NATURE COLUMN
Max Henrici
THE ROLE OF TAPE
James E. Corbin — Lewis W. Lehr
A FUNCTIONAL WAY OF TEACHING PHYSICS O. A. Nelson
ACIDITY AND BASICITY IN ORGANIC SOLVENTS Marion Maclean Davis
THE RARE EARTH ELEMENTS—A NEGLECTED PHASE OF INORGANIC CHEMISTRY
Therald Moeller
POLYELECTROLYTES AS SYNTHETIC SOIL CONDITIONERS
DETECTION AND EVALUATION OF HEARING IMPAIRMENTS Thomas J. LePine
THE WORK OF THE COMMITTEE ON DIAGNOSTIC READING TESTS, INCORPORATED

In Future Numbers . . .

Among the articles planned for publication in the near future are:

Reading in Mathematics

By Catherine A. V. Lyons, Department of Mathematics, Perry High School, Pittsburgh, Pennsylvania.

The Transistor

By R. D. Lohman, Radio Corporation of America, RCA Laboratories Division, Princeton, New Jersey.

Solar Energy for the Production of High Temperatures By Gene Braught, St. Louis, Missouri.

Science and Society

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Formaldehyde, Its Chemistry and Application

The Committee

By Alan K. Jeydel, Chemical Division, Celanese Corporation of America, New York City.

A Chemical Show for Younger People

By James O. Thompson and Edgar E. Dickey, Research Chemists, The Institute of Paper Chemistry, Appleton, Wisconsin.

The Family of Brasses

By Carl H. Pihl, Copper and Brass Research Association, New York City.

An Un-academic High School Physics Course

By Brother Gabriel, F.S.C., Central Catholic High School, Pittsburgh, Pennsylvania.

Colloids from the Sea

Earl C. Jertson, President, Seaplant Chemical Corporation, New Bedford, Massachusetts.

SEVENTY-SEVEN

Putting the "Bugs" to Work

• By Joseph Bonnano

MEDICAL AND PHARMACEUTICAL INFORMATION BUREAU, NEW YORK CITY

Almost everyone now knows of the hormone cortisone and of its great value in the treatment of rheumatoid arthritis and other serious maladies.

The complex problems involved in its production, and the consequent high cost have limited the free use of this "wonder drug."

Now a way has been discovered to shorten the manufacturing process, increase the supply, and reduce the cost. "Bugs" have been put to work.

There are two to three million persons in the United States suffering from rheumatoid arthritis, the most painful and crippling form of one of the nation's most chronic diseases—a disease that strikes 400,000 each year.

Real hope for rheumatoid arthritis patients came in 1948 when it was discovered that hormones derived from the adrenal glands (two triangular bits of tissue on top of the kidneys) could be used to relieve not only rheumatoid arthritics but persons with rheumatic fever, ulcerative colitis, asthma, eye diseases, and a score of other maladies.

One of the most effective of these adrenal hormones is cortisone. How cortisone and the other hormones derived from the adrenal glands work to relieve rheumatoid arthritis is a medical mystery; but they do suppress the inflammatory reaction associated with the disease, thus keeping rheumatic joints free of scar tissue that would limit motion.

Mystery or not, cortisone helps rheumatoid arthritis sufferers. Stories of its beneficial effects paralleled the penicillin wonder drug stories of the past decade. But there was a serious drawback that put a dampener on the adrenal hormone development. Cortisone, and its companion drug, ACTH, were expensive, worth several times their weight in gold.

The reason was the complex production problems involved. Cortisone, for example, was made from a component of cattle bile called desoxycholic acid. Bile from 40 head of cattle was needed to provide enough cortisone to treat just one patient for just one day.

That was only part of the production problem. Even with an abundant supply of desoxycholic acid, it still had to be converted into cortisone. This was a tough job since the only link between the acid and cortisone is their somewhat similar basic chemical structure. The caterpillar-into-butterfly process involved no less than 37 steps, but as the medical researchers put it, "the first 17 steps are the hardest," for these involve juggling an atom of oxygen into what is known as the eleven-position, while unseating two hydrogen atoms, the former occupants of the key spot.

Here, then, seemed to be the crux of the problem: find a new starting material with the oxygen atom already in the eleven-position, thereby eliminating most of the complex production steps, and the cattle; the ultimate goal of more cortisone at less cost will then be reached.

With the objective clearly in view the pharmaceutical industry, like a big-city police department, turned up clues, screened "suspects," and checked all leads no matter how slight the chance of success.

Following a strong lead, The Upjohn Company, a Michigan drug firm that had pioneered in adrenal hormone development, participated in a six-month African expedition in search of a "lost" vine that had the desired chemical structure. Unfortunately, the Dark Continent shed little light on cortisone production problems, and the expedition returned empty-handed.

Meanwhile, in addition to the search for a better starting material, the pharmaceutical industry explored other possibilities, including:

- 1. Improvement of the existing bile acid process (this succeeded in cutting the steps to about 20 but the difficult 17-step oxygen shift remained).
- Development of a total synthesis of cortisone using a common chemical like benzene.
- Development of a method utilizing enzymes (organic compounds that help to speed up or produce a change) from the adrenal gland itself.

These experiments showed varying degrees of promise and success, particularly in the development of Compound F, a powerful sister-drug of cortisone. But the big cost-production problem remained.

All research roads at Upjohn led to the belief that the best chance of producing cortisone cheaply and in quantity lay in mobilizing microbes to by-pass the complex chemical process. Scientists reasoned that if the micro-organisms in mold could be used to produce antibiotics like penicillin and streptomycin, the "bugs" might be put to work doing a similar job for cortisone.

Thousands of molds were screened to find the hormone closest to cortisone. The break came when a growth was noticed in a dish set by an open window to obtain mold samples. The mold was of the genus *Rhizopus*, a distant cousin of the bread mold.

The Upjohn team found that when Rhizopus mold is placed in a chemical "soup" with starting materials derived from such abundant substances as soybeans, yeast, or Mexican yams, the bugs perform the once-complicated oxygen shift in a single fermentation step.

The method is successful, not only in cortisone production but in the production of Compound F, and another similar drug, Compound B.

By putting bugs to work, then, Upjohn was able to eliminate a costly chemical production process, and more important, was able to make cortisone more widely available to arthritis sufferers everywhere.

Chelating Agents

• By Harold Narcus, Ph.D.

PRESIDENT AND TECHNICAL DIRECTOR, ELECTROCHEMICAL INDUSTRIES, INCORPORATED, WORCESTER, MASSACHUSETTS

This paper is an easily understood discussion of a newly developed class of organic compounds that are becoming increasingly important in several industrial fields.

A consideration of sequestration precedes the study of chelating agents. These "claw-like" compounds are finding applications in water softening, scale removal, fat saponification, and the removal of metallic impurities.

Because of the limited amount of reference literature available, particularly in this country, dealing with the chemical and physical properties of chelating agents, the purpose of this paper is to bring to light some of the potentialities of these newly developed organic compounds. This treatise discusses first the more familiar sequestering agents; secondly, the commercial chelating agents, making a comparison between the two; and finally the present applications for chelating agents.

The information herein is presented in such a way that a profound knowledge of physical or organic chemistry is not a requisite for a complete understanding of the behavior of these compounds.

Sequestering Agents

It is best to begin by reviewing the chemical and physical behavior of the more common sequestering agents so that a satisfactory differentiation may be made between these and the less-known chelating agents.

The reader has, without doubt, encountered the term "sequestering agent" on numerous occasions, especially during his perusal of technical literature dealing with methods for softening water. Perhaps these compounds were met with in the literature describing methods for counteracting the adverse effects of heavy metal ions such as those of Cu⁺⁺, Ni⁺⁺, Co⁺⁺, and other divalent ions or those of the common alkali earths such as those of Ca⁺⁺, Mg⁺⁺, Ba⁺⁺ and Sr⁺⁺.

Actually, sequestration, in which chelation will be shown to be incorporated, is of comparatively recent origin. According to the dictionary, it means "the act of taking possession of by confiscating or appropriating." Chemically, it is the reduction of the concentration of a polyvalent positive ion (a Ca^{++} , for example) in solution by combination with a negative ion [like a $(PO_3)_6=$] to form a different complex negative ion (in this instance, a complex calcium metaphosphate ion, $Ca(PO_3)_6=$. The ultimate result is that the re-

maining concentration of the positive, polyvalent Ca++ is so low that it will not be precipitated by a given negative ion which normally would precipitate calcium, such as an oxalate ion. In other words, if you add an oxalate ion to a completely sequestered calcium solution no calcium oxalate will precipitate. Removal of calcium hardness from water-more commonly termed "watersoftening"-is a well-known example of this chemical phenomenon. Sequestering agents such as sodium metaphosphate are actually water soluble ion exchangers, and their employment in water softening is an excellent example of the principle of sequestration. Fortunately, the quantity of agent necessary to carry out the combination described can be accurately determined. This "sequestration" value is the quantity of sequestering agent required to combine with or "sequester" a unit quantity of the polyvalent positive ion and form with it a complex negative ion which is stable against precipitation by a known precipitant for that particular polyvalent positive ion. This is a definite chemical value, better termed a stoichiometric value.

Experiment to Illustrate the Principle of Sequestration

To each of two 1000 c.c. beakers (A) and (B) add 500 c.c. of distilled water and 9½ c.c. of a solution containing 10 grams of anhydrous calcium chloride per liter (1% solution of calcium chloride). Each beaker will then have water with a calcium hardness of 171 parts per million, or 10 grains per gallon.

To beaker (B) only, add 6 c.c. of a 5% sodium metaphosphate solution (such as "Calgon").

Adjust the pH of both solutions (A) and (B) to 8.2 with 10 c.c. of a 10% sodium hydroxide solution.

Add $10\ \text{c.c.}$ of a standard soap solution (1 c.c. is equal to 1 mg. of calcium carbonate) to both solutions.

Upon stirring the solution in both beakers it will be noted that there are no suds in Beaker (A), but copious suds formation in Beaker (B).

The sodium metaphosphate has sequestered the calcium ion in (B) preventing it from reacting with the soap to form an insoluble calcium soap, thus leaving the sodium soap free to form its characteristic suds. If additional 5% solution of sodium metapsosphate (about 10 c.c.) is added to Beaker (A) the calcium soap precipitation will re-dissolve and suds will be produced as in Beaker (B).

In the process of sequestration, the polyvalent positive ion (such as the calcium ion) has practically disappeared from the solution without being evolved as a gas, removed as a precipitate, or deposited as an element, as in electroplating. In other words, the Ca++ ions are still in solution but the chemical characteristics normal to their simple ions are gone.

Graham's Salt (NaPO₃)_n, (where "n" equals the number of NaPO₃ units common to the polymeric molecule in solution) is a well-known commercial sequestrant and, chemically, is a neutral sodium metaphosphate. It is considered to be an efficient sequestering agent having many industrial applications.

The chemical reaction involved in this process of sequestration best illustrates the action of all polyphosphates and is as follows:

$$\begin{array}{c} \cdot \ \ \mathrm{Na_{2}[Na_{4}(PO_{3})_{6}]} \ + \ \mathrm{Ca^{++}} \rightarrow \ \mathrm{Na_{2}[Na_{2}Ca(PO_{3})_{6}]} \\ + \ 2 \ \mathrm{Na^{+}} \\ \mathrm{(or)} \\ \mathrm{Na_{2}[Na_{4}(PO_{3})_{6}]} \ + \ \mathrm{Ca} \ \mathrm{CO_{3}} \rightarrow \mathrm{Na_{2}[Na_{2}Ca(PO_{3})_{6}]} \\ + \ \mathrm{Na_{2}CO_{3}} \end{array}$$

We have seen in this treatment of hard water with Graham's Salt (as illustrated in the previous experiment) an ion exchange similar to the base exchange reactions of zeolites, but occurring entirely in solution, each positive calcium ion replacing two sodium ions in a complex negative ion. To prove that the residual calcium ion concentration is extremely low we can add soap, which normally forms a very insoluble salt with calcium ions but will not precipitate this insoluble calcium salt when sufficient Graham's Salt is present. We are most familiar with this insoluble soap formation in soap burnishing when insoluble, sticky precipitates form with hard water. Conversely, Graham's Salt will dissolve precipitated calcium soaps.

It is important to point out again that no calcium actually has been removed in this sequestration process by volatilization, plating out, or precipitation, and a true solution remains. Still, the calcium ion is no longer present in more than a minute amount (of the order of a few parts per million). This, therefore, reveals the basic principle of "sequestration." Actually, in this process, the calcium ion has lost its chemical or "ionic" identity.

The sequestration of the calcium ion as described is affected by the pH of the solution but is not primarily a pH effect. Thus, calcium carbonate will dissolve in acid and not in alkali, but it can be made soluble in alkaline solution by the addition of an addition agent such as neutral sodium metaphosphate.

Other divalent metal ions can likewise be sequestered to a greater or lesser degree; for example, ions such as Ba++, Sr++, Mg++, Fe++, Co++ and Ni++. Furthermore, trivalent ions such as Fe+++, Al+++, etc. are sequestered, but to a lesser degree than the divalent ions, and do not appear to be so tightly held in a complex negative ion. Unstable complexes result with the heavier monovalent cations such as silver.

This sequestration phenomenon is not just a laboratory curiosity but rather has found wide commercial applications. As previously noted, it is principally employed in the softening of water which is to be ultimately used with soap. It is a well-established fact that water good enough for drinking is not necessarily good enough for use in processes such as electroplating. All natural water, with the exception of rain water, contains some calcium and magnesium ions (the parts per million varying in different geographical locations) and these ions of calcium and magnesium form insoluble precipitates or scums with soap-a most objectionable factor in the subsequent electroplating of metals. Insoluble scum or film formation on work which has been burnished is an objectionable occurrence known to all in the metal finishing field.

Before a soap can form a good lather, which is an attribute of the alkali metal soaps, it must be first added in sufficient amounts to precipitate the calcium and magnesium ions, these being the so-called water "hardness" constituents. By employment of a suitable sequestering agent such as sodium metaphosphate this precipitation can be prevented, and a lather formed with considerable less soap.

Other sequestering agents are known, but are active to a lesser degree. Reference is made to sodium pyrophosphate, tetra sodium pyrophosphate, sodium tetraphosphate and sodium tripolyphosphate.

One disadvantage of all polyphosphates is that the higher the concentration of the water hardness salts, the lower the efficiency of the polyphosphates. This is not true in the case of the chelating agents now to be discussed.

Chelating Agents

With this preliminary discussion, we are now more fully prepared to cope with the term "chelating" agent and the principle of chelation. The main differences between the previously discussed sequestering agents and the chelating agents will become evident. It may be stated here, however, that the chelating agents generally concern themselves more in the realm of organic chemistry than the sequestering agents, which we normally consider inorganic in their chemical characteristics.

Chemically, a chelating agent is a compound which will inactivate a metallic ion by forming an inner ring structure in the molecule, the metallic ion becoming part of the ring. A sequestering agent is any complexing compound which forms a water-soluble metal complex compound.

Around 1948, a compound known as Trilon A was investigated. This compound had the following structural formula:

$$\begin{array}{c} CH_2COONa \\ N-CH_2COONa \\ CH_2COONa \end{array}$$

From this organic structure resolved the modern chelating agent, Trilon B:

NaOOC • CH
$$_2$$
 CH $_2$ COONa
NaOOC • CH $_2$ CH $_2$ COONa

This compound² is the tetra sodium derivative of a synthetically prepared polyamino acid, ethylene diamine tetraacetic acid. There are now commercially available various types of chelating agents known as Versenes³ and Sequestrenes⁴ having the forms shown in Table I.

The polyamino acid, ethylene diamine tetraacetic acid (EDTA), is only slightly soluble in water, but its sodium salts are more readily soluble. For example, the disodium form of EDTA is 3% soluble in water, and the tri- and tetra-sodium forms of EDTA are highly

Table I-Various Forms of Chelating Agents

soluble. Commercially, the EDTA and its sodium derivatives are available as white, non-hygroscopic crystalline powders. The tetra-sodium derivative of EDTA is also available as a colorless liquid.

The EDTA has a pH of 2.8 while its di-, tri and tetrasodium salts have pH's of 4.8, 8.8 and 10.5 respectively:

Figure I shows the existence in solution of the various salts of ethylene diamine tetraacetic acid resulting when base is added to a stirred suspension of EDTA.

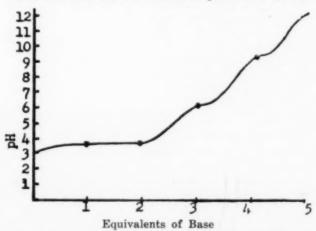


FIGURE 1. Formation of various forms of EDTA by addition of base.

The reversibility of the reaction involved is shown in the following chemical reaction:

$$\begin{array}{c} OH^-\\ H_4Y \underset{H^+}{\rightleftharpoons} NaH_3Y \underset{H^+}{\rightleftharpoons} Na_2H_2Y \underset{H^+}{\rightleftharpoons} Na_3HY \underset{H^+}{\rightleftharpoons} Na_4Y \end{array}$$

in which "Y" is a simple way to represent the ethylene diamine tetraacetic acid residue from which four protons have been removed. It signifies a terminology adopted by investigators in the field of chelation.

These chelating agents in the variety of chemical forms are not actually conventional sequestering agents, such as the polyphosphates previously discussed. In spite of widespread industrial use, they have received very little attention in the technical literature published in this country. Investigators^{5, 6, 7} in Germany and Switzerland, however, have studied these materials and related compounds very thoroughly, and their findings are just beginning to appear in English in this country. Presently, there are at least two companies^{3, 4} manufacturing these organic chelating agents and their derivatives on a commercial scale in this country and they are available at reasonable prices.

These substances, because of their special nature, are termed organic chelating agents rather than the more general term of organic sequestering agents or sequestrants. As will be shown presently, they form inner salts or chelate complexes which account for their chemical behavior in solution. While chelating agents have most of the properties of the ordinary sequestering agents, they form more stable reaction products, known as the chelate of the metal, and these chelates are quite stable over a wide range of pH; they are not decomposed by either weakly acid or highly alkaline solutions. Temperature, time and the addition of common precipitation agents have no effect on these chelated metal ions. On the other hand, sequestering agents do not actually form this stable a complex, but rely on the dispersion action of the reagents. Coagulation is prevented by the sequestering agent to achieve the desired result, but eventual coagulation may take place gradually. The polyphosphates excel the chelating agents only in "threshold effect"-that is, the polyphosphates temporarily inhibit precipitation of a metal ion even though there is not enough polyphosphate present to completely complex the metals present. This phenomenon, which is not an attribute of chelating agents, is probably due, as stated, to physical dispersion.

The sodium salt of EDTA has been shown to be four time more effective than the inorganic polyphosphates. It is not recommended for use in strong oxidizing solutions since it will be oxidized to a cyclic structure. Permanganates and hot acid dichromates will bring about this change in the chemical structure of the compound. Sulfides will also break up the chelate formation because of the solubility products of sulfides, which are of such a magnitude that precipitation is favored.

These organic chelating agents have the ability to form soluble non-ionic chelates with such polyvalent ions as Cu++, Co++, Ni++; Zn++, Fe+++, Al+++, etc. The result is a complete change in the property of these ions in solution. In other words, as in the process of sequestration, chelation prevents the metal ions from being precipitated by common agents which under normal conditions would cause precipitation. For example, the Ca++, will not be precipitated by an oxalate-

(Continued on Page 104)

Writing a Nature Column

By Max Henrici

NATURE EDITOR, THE PITTSBURGH SUN-TELEGRAPH, PITTSBURGH, PENNSYLVANIA

Regardless of where they are located, teachers of the natural sciences need never lack for illustrative material. Here is encouragement to use whatever is available. And much is to be found close at hand if it is sought seriously.

Mr. Henrici, one of the country's distinguished Nature columnists, is a patient and skilled observer, but he is not a trained scientist. He relates how he began to write about Nature, and where he finds material for his column.

In the autumn of 1934 Dr. Thomas D. Howe, professor of botany at Duquesne University, made a survey of the flora on the campus or in the immediate vicinity of the university. He found 44 species of vascular plants. Many were weeds introduced from the Old World, but even these were of interest. There were, for instance, some grasses rare in Western Pennsylvania, among them Jungle Rice (Echinochloa colona), a Bristly Foxtail Grass (Setaria verticillata), and a Moor-Grass (Molinia caerulea) from Europe which, although known to have established itself along the Atlantic seaboard, had not previously been recorded from so far inland. What was regarded as a particularly notable find was Aster Pringlei, uncommon in our region, and mostly limited to rocky banks and bluffs.

I mention these many interesting plants found by a trained observer within a short distance of Pittsburgh's business district as an answer to those who ask where the writer of a Nature column can find material to keep it going, day after day, year after year. The available material is overwhelming in its vastness. The problem is, not where to find a subject, but how to choose from among the myriad of subjects that claim consideration.

Right in the heart of the downtown business district one finds every now and then some surprising bird, mammal or insect to remind us how close we are at all times to Nature. On the afternoon of December 22, 1941, a duck hawk (Falco peregrinus), the peregrine of falconry, was observed on the cornice of one of Pittsburgh's taller office buildings in the act of devouring a pigeon. It was photographed with a telephoto lens, and the picture left no doubt of the bird's identity. During the succeeding three months it was frequently observed by students of ornithology on the Arrott Building, on the First National Bank Building, and in flight over Fifth Avenue at Grant Street.

Sparrow hawks (Falco sparverius) nested and raised young during the summer of 1934 in an arched opening at the summit of the west facade of the Granite Building, at Sixth Avenue and Wood Street, in downtown

Pittsburgh. They were carefully studied and photographed.

I myself have found nighthawks (Chordeiles minor) raising young on the flat roof of the Sun-Telegraph Building in Telegraph Square.

I cite these as examples of the fact that even in what might at first thought appear to be a most unlikely locality in which to look for fauna and flora—the commercial section of a large industrial metropolis—species of great interest to the Nature columnist, the science teacher, and people generally, can sometimes be found.

But when one goes into the suburbs, and especially a rural area like McAllister's Cross Roads, about 20 miles from Pittsburgh, where the present writer lives, the variety of plants and animals to be seen, studied, and written about, is seemingly infinite.

In the category of mammals alone I have observed within a quarter of a mile of my home during the 25 years of my residence there the Virginia opossum (Didelphis virginiana), the hairy-tailed mole (Parascalops breweri), the short-tailed shrew (Blarina brevicauda), the Eastern raccoon (Procyon lotor), the New York weasel (Mustela frenata), the Eastern skunk (Mephitis nigra), the Eastern red fox (Vulpes fulva), the Southern groundhog (Marmota monax), the Fisher chipmunk (Tamias striatus), the Southern red squirrel (Tamiasciurus hudsonicus), the Northern gray squirrel (Sciurus carolinensis), the Eastern flying squirrel (Glaucomys volans), the Northern white-footed mouse (Peromyscus leucopus), the common muskrat (Ondatra zibethica), the cottontail rabbit (Sylvilagus floridanus), the Virginia deer (Odocoileus virginianus), and bats which I was unable to identify.

In a nearby brook, in a single afternoon, I collected these species of fish: Red-sided dace (Clinostomus elongatus), blunt-nosed minnow (Hyborhynchus notatus), black-nosed dace (Rhinichthys atronasus), stone roller minnow (Campostoma anomalum), common shiner (Notropis cornutus), cavern-jaw minnow (Ericymba buccata), creek chub (Semotilus atromaculatus), fantail darter (Poecilichthys flabellaris), and common sucker (Catostomus commersonnii).

Having, I hope, established my point that there is no limit to the number of species of fauna and flora open to observation even in the vicinity of a big city, I will not weary the reader further with lists of the hundreds of plants, birds, insects, reptiles, and specimens of plant and animal fossils that I have personally observed and collected in the neighborhood of my home.

I am not a biologist but a professional journalist who entered the profession as a reporter on a Pittsburgh daily newspaper in 1904. How, when I was well along in years, I came to start writing a Nature column, may be of interest.

(Continued on Page 107)

The Role of Tape

• By James E. Corbin, B.S., (St. Thomas College)

MANAGER, TECHNICAL SERVICE, TAPE DIVISION, AND

Lewis W. Lehr, B.S. in Ch.E., (University of Nebraska)

ASSISTANT MANAGER, TECHNICAL SERVICE, TAPE DIVISION, MINNESOTA MINING AND MANUFACTURING COMPANY, ST. PAUL, MINNESOTA

Few who use the Scotch brand of cellophane tape so freely every day realize that it is only one of a large family of pressure-sensitive adhesive tapes that have become indispensable in industry as well as in the home, the office, and the school.

Tapes are made of many different kinds of material and their various backings are especially designed for the uses to which the tape is to be put.

This article discusses the composition and uses of various kinds of tape, and relates how this important industry has developed within the past twenty-five years.

Tradition has it that Henry Ford once said, "Any customer can have a car painted any color that he wants so long as it is black." This situation might still be true today; or, at any rate, brightly painted cars would be priced exorbitantly high were it not for the invention of two new products around 1925.

Only a few short years later, two remarkable inventions proved "Henry" wrong. Sprayable quick-drying finishes allowed fast color application with short drying cycles. This solved one problem but created an-

other. How to spray a car and not drip paint over the trim, upholstery, etc., loomed up as an almost impossible situation. It was then that Minnesota Mining and Manufacturing Co., an abrasive manufacturer, provided the solution in the form of the second remarkable invention—pressure-sensitive masking tape. It provided a means of holding a masking paper securely in place, and supplied a clean straight edge for fast "two-tone" color painting.

As the auto industry grew, so grew the demands on this "granddaddy" of all tapes. Its properties were improved; new tapes were needed and developed; and other potential applications began to appear in industries other than automotive.

During the first decade of masking tape, another outstanding development occurred. The technology of organic chemistry improved rapidly, and from it came cellophane, the first economical transparent synthetic film produced commercially. Shortly after this, the 3M Company discovered a water-clear pressure-sensitive adhesive and found a way to combine this with cellophane, in a roll that could be unwound: thus providing the first transparent pressure-sensitive adhesive tape—cellophane tape.

These first two tapes, one having a treated paper backing; the other, a synthetic film, were the forebearers of today's more than 300 varieties of pressuresensitive tapes.

Before these tapes are further considered, the question may arise, "What exactly is a pressure-sensitive adhesive tape?"

Generally, it is defined as a flexible backing coated

with a permanently and aggressively tacky adhesive so composed that it sticks instantly and tightly to surfaces against which it is pressed. It is ready to use at any time. Pressure-

LEFT—"Scotch" brand No-Mar protective tape is finding widespread use by industry for protecting finished stainless steel sheeting during handling and processing. Here, a wide strip of the tape is shown being applied to a sheet of stainless steel.

CENTER—Another tape finding widespread use in the printing industry is "Scotch-Weld" bonding film which is used in place of nails and glue for mounting halftone plates to blocks. Platemaker in this photo is shown removing the protective liner from a piece of the film.

RIGHT—Though there are probably thousands of identifying uses for pressure-sensitive tapes, one outstanding widespread use today is the use of "Scotch" brand plastic film tape for lane marking in the nation's industrial plants. Here, a maintenance man is shown applying a strip of the tape to his plant's floor. Tests show that stripes made with the tape will outlast conventional paint markings five to one.

-Photos Courtesy Minnesota Mining & Manufacturing Co.







sensitive adhesives are so firm that the tape can be unwound from rolls and removed from smooth surfaces without transfer of the adhesive. These tapes can be handled without gumming the fingers, and they can be used in mechanical dispensers and applicators without fouling the mechanism. With this rather broad definition, it is easy to visualize the possibilities which have made 300 tapes a reality.

Consider first the backing. Its limitations are only those of flexibility and strength sufficient to withstand the action of the adhesive in unwind. Today's tapes incorporate many different backing materials. Papers, specially treated, are the most common. These may be of various weights and creped for curved paint masking and good contour conformability, or of flatstock for strength and toughness.

The second large category of pressure-sensitive tapes is that group which uses a synthetic or plastic type backing. The most well-known in this group is cellophane. Its transparency, ease of handling and dispensing, and moderate price have made it the symbol of pressure-sensitive tapes. Because this film has short-comings which make it impractical for some applications, newer films have been substituted. Cellulose acetate, a moisture resistant, transparent film, is an example.

There are many other tapes utilizing plastic backings. The vinyl compounds have contributed heavily in this group. Vinyl films have toughness, strength, stretch, conformability, weather resistance, and moisture vapor resistance, all much better than cellophane. Their electrical insulation properties are excellent; they can be compounded in colors; they can be calendered or cast in varying thicknesses.

Polyethylene plastic has similar characteristics, and tapes made from it find similar usage. Other newcomers in the field of plastic films are constantly being investigated and adopted for use as tape backings. Each has special properties which satisfies a need and thus create the demand.

There is a third group of tapes made from backings which can probably best be termed as miscellaneous. This group includes cloths of cotton, glass and acetaterayon—both treated and untreated. So, too, have the metal foils—copper, aluminum, and lead—been used as backings.

The list of backing materials is not yet complete. Whether it be paper, plastic, cloth, or metal foil, certain specific needs have proved them inadequate. Where the individual backings have failed, the tape industry has combined them into laminates. These laminates thus become the backings for new tapes with new and improved characteristics. Through the use of this method have come the acetate-fibre tapes—those made from a laminate of thin cellulose acetate for chemical stability, and a tissue-like paper for physical stability. So, too, have the acetate film and cloth, foil and paper, and cellophane film and fibre tapes been developed.

Even these, though, have led to a very new and remarkable group of tapes—the paper-filament and acetate-filament tapes. In these tapes the backing is composed of rayon or glass filaments lineally aligned and held together by an adhesive which bonds them to

either cellulose acetate or paper. These filaments provide lineal strength in tapes far beyond the dreams of a decade ago.

As interesting and varied as all of these tape backings are, they alone do not make a pressure-sensitive tape. The name denotes the other very important component—pressure-sensitive adhesive. Most adhesives are composed of rubber which has been softened through mechanical action and made sticky or tacky by the addition of certain resins. Here again, though, the number of adhesives is nearly endless. Both natural and synthetic rubbers, combined with various resins, as well as antioxidants and pigments, provide adhesives having the desired properties for many special applications.

With all the combinations of backings and adhesives possible, an almost limitless variety of end uses can be readily visualized. Thus, pressure-sensitive tapes today have become recognized as one of the most important tools of industry as well as a boon to the homemaker.

The uses for tapes have been classified into the following general categories: masking, holding, reinforcing, sealing, protecting, splicing, and identifying.

Masking

Paint masking, which was the necessity that fathered the invention of pressure-sensitive tapes, continues to be one of the broadest outlets. In the automotive industry as well as in automotive repair shops, as examples, tapes are used to mask off chromium trim, windows, rubber moldings, and upholstery during spray painting. The adhesives so used must possess sufficient tack to adhere to these various surfaces and yet be removed from them without discoloring or transferring to them after high temperature drying of the paint. Simultaneously, the backing must be chemically impermeable to the paint solvents, strong enough to support heavy paper aprons, and yet have sufficient stretch to conform to irregular surfaces.

Similar applications are found in other industries which do spray painting—the aircraft industry, the furniture industry, and the appliance industry.

Entirely different requirements for masking exist in the electroplating field where tapes are used to prevent buildup of plating metal on certain areas of the article being plated. As vinyls are resistant to the hot alkalies and acids of the electroplating baths, this is the backing commonly used for such tapes.

Beside masking for chemical protection, tapes are also used to mask off for abrasion protection. A heavy rubber-like backing coated with a high tack adhesive is used to mask stone and glass during sandblasting operations.

Holding

Shortly after the introduction of tape for masking, a new use was found for it—that of holding. This was the field which led to the development of the strong, non-stretchy flatback-type paper tapes. Appliance manufacturers found pressure-sensitive tape to be ideal for holding doors shut and movable parts in place on refrigerators and stoves during shipment. As the early tapes had a tendency to stain the enamels used on

these appliances, new non-staining adhesives having strong bonding power to prevent slippage and loosening were developed and incorporated into these holding tapes.

Today there are many more holding applications. Through the use of special tapes the outer laps of rolled goods from adding machine paper to coiled sheet metal are firmly held secure. Another special tape temporarily holds rivets in rivet holes for the aircraft industry during fabrication. Another holds valuable coins and stamps in their proper place in collections.

Tapes having a paper backing with adhesive on both the back and face side have replaced nails in holding half-tone plates to wood blocks in the printing industry. These same double coated tapes hold hat bands in place on straw hats. The binding on insoles of women's shoes are similarly held in place.

Reinforcing

As tapes were improved and new ones developed for holding, they soon found their way into the reinforcing field. Chief among these is carton reinforcing. Today the "filament tapes" having tensile strengths up to 500 pounds per inch of tape width are being used in place of steel banding to reinforce fibreboard shipping cartons. These same filament-type tapes are used to reinforce the plastic, and support the instrument gondola of stratospheric weather balloons.

Edge reinforcement of blueprints, and similar much used papers, is achieved through the use of the tough acetate fibre tapes. These tapes are mechanically applied over the edges of these papers to prevent edge tearing and increase the use life of the papers up to ten times.

Sealing

Since pressure-sensitive adhesives form such an intimate bond with the surface to which the tape is applied, they naturally fall into widespread use for many types of sealing. The choice of backing can be widely varied to provide the type of barrier required.

Lead foil and aluminum foil tapes provide the most positive barrier against moisture vapor penetration. These tapes have thus been used to seal thermo-type windows and to seal the seams between the panels in cold storage vaults.

The plastic film tapes, such as vinyl and polyethylene, are also good barriers and because of their good stretch characteristics readily conform and seal caps on bottled chemicals and medicines.

In the Armed Forces the acetate-fibre tapes are used as a vapor-proof carton seal for overseas shipments. The cartridge ejection slots under the wings of fighter aircraft are sealed with a similar tape to prevent dust and mud from blowing into the gun mechanism during take-off.

Transparent and colored cellophane tapes are used to seal many small retail packages of various types.

Protecting

Pressure-sensitive tapes are used to protect many types of surfaces from both mechanical and chemical action. Highly polished sheets of stainless steel are protected during shipment and fabrication by thin tough paper tapes. Chemically resistant vinyl tapes are used to wrap pipes in chemical plants where fumes would normally cause corrosion of the metal.

Splicing

In industries such as the manufacturing and treating of cloth, paper, and plastics, where high speed operation is essential to efficiency, the splicing at breaks in the web or the splicing of one roll to another creates problems. Because pressure-sensitive tapes adhere immediately and are easily adaptable to automatic application, they are valuable tools in this field. Many different types of tape are used, depending on the strength needed, the type of material being spliced, and the subsequent mechanical or chemical processing which may follow the splicing.

An entirely different aspect of splicing is found in the electrical industry. Specially formulated vinyl tapes have generally replaced the old-fashioned combination of friction and rubber tape for splicing electrical wiring. The high dielectric strength of the vinyls provides excellent electrical insulation, and their chemical stability gives semi-permanent splices which resist deterioration under severe weathering conditions.

Identifying

Because tapes are available in a wide variety of colors and are capable of being printed, they are widely used in identifying and labeling. The more familiar type of printed labels are those used on Christmas packages and those used for oil-change labels in garages and filling stations, but many other such tapes are specially printed to carry advertising messages or directions-for-use messages.

Colored tapes find wide usage as a method of identifying or coding. They may be found on file cabinets, on sales executives' charts, or even as identification on the various fluid lines in aircraft.

Because paint wears away quickly and dries slowly, tape is being used on floors for identifying traffic and storage lanes. Similarly, it is used to outline basketball and volleyball courts in gymnasiums.

Miscellaneous

Hundreds of other uses which cannot be classified under the above categories are found throughout industry. The use of lead foil tape as an antenna on helicopters; the use of colored plastic tapes for striping; and the use of luminescent tapes for identification in darkness are illustrations of these miscellaneous types of usage.

Pressure-sensitive adhesive tape, the novelty of yesterday, has today become the tool of home, school and industry. Its use has resulted in hundreds of thousands of dollars of labor-saving every year and has made possible efficiencies in production never before achieved. Existing tapes, as well as those yet to be developed, will play a key role in the scientific advancement of tomorrow.

A Functional Way of Teaching Physics

• By O. A. Nelson

PRINCIPAL, WILSON HIGH SCHOOL, SAINT PAUL, MINNESOTA

Many school administrators are concerned at the increasing lack of pupil interest in high school physics.

Here is definite proof that interest can be aroused by a different method of teaching. It has been done.

A better idea of the character of the course may be gained from Mr. Nelson's two books recently published by Ginn & Co. They are: "Everyday Physics" and "Workbook and Laboratory Manual for Everyday Physics." Dr. John G. Winans of the department of physics of the University of Wisconsin is co-author of "Everyday Physics."

In the opinion of most high school teachers, and perhaps all pupils, physics is one of the most difficult subjects in the curriculum.

Some instructors pride themselves in making the course so difficult that only the pupils with strong science interest and aptitude care to take the subject. So much technical material and mathematics are included that much more time is usually necessary to complete a science assignment than one given in another subject.

The writer does not question the fact that physics can be, and is, made difficult. But in doing so what is gained?

- (1) Do we teach pupils the physics they can make use of in their daily living?
- (2) Do we make better students (scientists) of the few that elect the subject?
- (3) Should the subject be for just the few, or can all pupils benefit from it in this technological age?
- (4) Do more pupils continue the study of physics in college because they were given a "stiff" course in high school?
- (5) Is the subject better understood because a large number of technical mathematics problems are worked?
- (6) Can pupils of low science aptitude understand and benefit from the study of physics?
- (7) When studying physics is there any value in following the old sequence of mechanics, heat, light, sound, electricity and electronics?

The writer has spent more than 30 years trying to find answers to these and a number of other questions. A large number of tests were given, interviews were conducted with former pupils and comparisons were made with results where formal instruction had been used. The following conclusions were reached for each of the questions:

(1) The subject can be taught in a much more functional way than that presented in the average text and in such a way that the material will be very much more useful to the pupils.

- (2) No. A functional course seems to have much more value.
 - (3) All pupils can benefit and should study physics.
- (4) No. Too many become discouraged before they learn to understand the subject.
- (5) No. Only by a few pupils who think in terms of figures; perhaps about five per cent.
- (6) Yes, definitely so. It would be too bad in this technological age if only the science minded individuals could understand science.
 - (7) None whatsoever.

For eleven years I attempted to find a better way of teaching physics, but with little success. A chance remark by a pupil helped develop a very different approach. At an after school session some time had been spent trying to explain Pascal's Law to a boy, but there seemed to be little or no progress. With the hope of better results the boy was asked to explain how a certain machine functioned, that his father used on construction jobs. The lad had operated the machine and knew how it worked. He explained it fully, including Pascal's Law expressed in his own words. He was then shown that his explanation and mine were the same. With a surprised look he answered: Why didn't you say so before? I know how that works!

Why had I not said so before? I had tried to explain physics as it was written in the text; as I had learned it at college. It was far above the interest level and ability level of the average pupil in the class. From then on, critical checks were made as to our method of teaching.

Whenever a recitation lacked interest or seemed too difficult for the pupils, the discussion was stopped and the questions asked: What is wrong now? What did I not say this time? The pupils were told the objectives of the lesson and were then asked what could have been done to make the lesson easier and more clear to them?

It was soon evident that they wanted two things. First, they wanted the discussion to start with some machine or problem that they knew something about; and second, they wanted words and terms used that they were somewhat familiar with so they would know what the instructor was talking about.

It took us about three years, with the help of the pupils and some of their parents, to build a course that contained all the laws and principles of science usually found in the average high school physics text. A great many practical applications not found in books were added. Technical mathematics problems were placed in mathematics classes where they belong. Over a period of another ten or twelve years, while the material was used in mimeograph form, it was improved considerably to make it even more interesting and worth while. The inductive method of teaching was employed

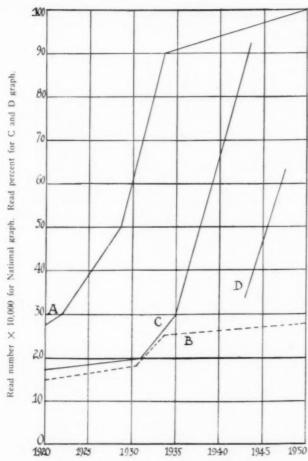


FIGURE 1. Enrollment in Physics in High School.

- Number of pupils graduating from all H. S. nationally. Number of pupils enrolled in Physics nationally. Percent of pupils enrolled in Physics in St. Cloud. Minn. Percent of pupils enrolled in Physics in Cent. H. S., St. Paul.

as much as possible. A number of the experiments used in the laboratory were developed by the pupils.

Over this period of time what were some of the results?

In 1929, when the writer started to teach in a certain school, 34 pupils were enrolled in physics out of a senior class of about 350. In 1930 and 1931, the numbers did not change materially. The change in the method of teaching was started during the school year of 1931-32. From then on the physics enrollment increased steadily until in 1942-43, the last year taught

at this school, 411 out of a graduating class of 456 had elected to study physics. This was 91 per cent of the class. In other schools where the writer has taught since that time the results have been somewhat similar. Figure I shows how this compares with national figures. Other instructors using the same method have had equally good results.

It is but natural that a number of questions will be asked when the change in subject matter and method is as great as that described above. Will the pupils be prepared to continue the study of physics in college? Yes. All evidence shows that they are better prepared. Without exception, the pupils who have been checked have done as well or better at college than they did in high school.

Second, is there enough "meat" in the course to challenge the very capable pupils? No text has material suitable for all who take the subject. Something must be done in all classes to meet individual differences. One way is to have the pupils give a large number of reports. In difficulty, the report must be geared to the ability of the pupil. This makes it possible for the most capable individual to be taxed to the limit of his ability. It is also necessary for the capable pupils to give their reports in such a way that the less capable can understand what is being talked about.

When the daily lesson was simple, the pupils that already understood the topic to be discussed were permitted to go to the library or laboratory to do additional work in which they were interested. In most cases this would be science work, but if the pupil had special interest in other fields this desire could be followed at times. Occasionally the less capable pupils would be sent to the library or laboratory if the instructor considered the material to be discussed far above the interest level or ability level of that group. Some might ask if the pupils would not miss important material when they were out of class. Of course they would, but they would gain in other ways, and it is hoped that this gain would compensate for what they missed in class. To be permitted to work at things in which they are most interested also serves as a reward for work well done. The pupils read more material outside of the text. This helps enrich later discussions in the classroom.

A common criticism of the kind of course discussed here is that it is just another "watered-down" physics. This is definitely not correct. It is physics written in such a way that it can be easily understood and therefore easily applied in life. Figure II gives the results

(Continued on Page 108)



Figure 2. The percentile score of a group of pupils on a standardized Physics test given at the end of the school year. All pupils had taken a course in Functional Physics during the year.

- 403 pupils were in the class. 246 pupils (61%) elected Physics. 204 pupils took the test.

Acidity and Basicity in Organic Solvents

By Marion Maclean Davis. Ph.D. (University of Illinois)

NATIONAL BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE, WASHINGTON, D. C.

All may not be aware of it, but acids and bases behave differently in organic liquids, especially liquid hydrocarbons, than they do in water. How they behave is important industrially as well as scientifically.

Dr. Davis has conducted revealing studies at the National Bureau of Standards, some results of which are reported in this article.

Your present ideas of acidity and basicity may be due for a change.

Until about 30 years ago, knowledge of acids and bases was restricted almost entirely to their behavior in aqueous solutions. Since that time, however, the rapid growth of the chemical industry has brought into common use a great variety of organic liquids that were previously unknown, or existed only as laboratory specimens. Among these are new lubricants, transformer oils, motor fuels, drycleaning solvents, automotive antifreezes, refrigerants, and solvents used in the molding of plastic articles.

In all these organic liquids—and especially in those which are hydrocarbons, such as lubricating oils and drycleaning solvents—acids and bases behave differently than they do in water. In some cases their effects are harmful; in others they are beneficial. It has thus become important to learn more about the behavior of acids and bases in organic solvents and to use this knowledge in developing methods for detecting their presence and for measuring the amounts present.

The National Bureau of Standards has a continuing program for the systematic investigation of acidity and basicity in organic liquids. This program was initiated 11 years ago at the request of industry and the armed services and is now partially supported by the Office of Naval Research. It has included a study of various techniques for measuring total acidity or basicity as well as relative acidic and basic strengths. New indicators have been developed which show the presence of acids and bases in hydrocarbons and other organic solvents by vivid changes in color, and information of fundamental importance to modern theories of acidity and basicity has been obtained. Of particular interest is the finding that various types of organic bases, in contrast to their more uniform behavior in water, show marked differences in their reactions with acids in an inert solvent.

When acids and bases dissolve in hydrocarbon solvents, they do not interact to any significant extent with the solvent to form ions. Consequently, it is not possible to judge the amount or the nature of a dissolved acid or base in such terms as conductance or pH. However, a dissolved acid will react with any sufficiently reactive base that is added; similarly, a dissolved base

will react with any sufficiently reactive acid. Much can then be learned by studying the resulting change in the properties of the solution. A particularly convenient procedure is to choose an organic dye as the added base or acid; when this is done, the extent of reaction can be determined by observing the shift in color as the dye is converted to a salt.

In order for a dye to be a useful indicator of acidity or basicity in a hydrocarbon, it must of course be sufficiently soluble in the solvent, and its colors before and after its conversion to a salt must be in sharp contrast. The dye must also be reactive enough to undergo a distinct change in color when only small amounts of acid or base are added, but it must not readily undergo side reactions such as alteration by light, or reaction with atmospheric oxygen or moisture. A few of the commercially available dyes used as indicators in aqueous solutions have been found to meet these specifications in part and have proved useful in organic solvents, but groups that have been introduced to make them water-soluble (the sulfonic acid group, for example) reduce their solubility in hydrocarbons and frequently lead to undesirable complications in their behavior.

It is thus necessary to develop a new series of indicators, comparable to those already available for aqueous solutions but tailored to fit organic media. With this objective, the Bureau has been investigating dyes, including some already described in the literature, which might be expected to have desirable properties. One of these compounds, bromophthalein magenta E (tetrabromophenolphthalein ethyl ester), has been found well suited to use as an organic indicator, and its reactions with different classes of organic bases in benzene and other organic solvents have been intensively studied.

$$Br$$
 C
 $O=C-OC_2H_5$
 $O+C$
 $O+C$

Bromophthalein Magenta E

Bromophthalein magenta E has been known for over 50 years, having been synthesized by German investigators during a period when the structures of phenolphthalein and related compounds were the subject of considerable investigation. However, its potential use as an acidic indicator in hydrocarbons was unknown

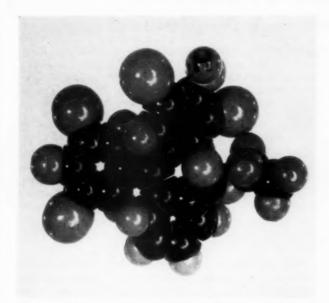


FIGURE 1. Molecular model of bromophthalein magenta E, showing the reactive hydrogen (marked "H") responsible for the color changes which make this compound of value as an indicator in organic solvents.

prior to the NBS studies. As the compound was not commercially available, it was necessary to prepare it in the laboratory. In the course of the work, detailed procedures for its synthesis were worked out.

Bromophthalein magenta E is much more soluble in hydrocarbons than bromophenol blue (the sulfonephthalein analogue which differs from bromophthalein magenta E in having a sulfonic acid group in the position occupied by the carbethoxy group), and it has the additional advantage of not being sensitive to atmospheric moisture. Bromophthalein magenta B (the *n*-butyl ester of tetrabromophenolphthalein), which had not previously been prepared, was also synthesized at the Bureau. As expected, this compound was found somewhat more soluble in hydrocarbons than bromophthalein magenta E but in most other respects very similar to it in behavior.

Bromophthalein magenta E gives a yellow solution in benzene or other hydrocarbon solvents. When a minute amount of an aliphatic amine or other organic base of comparable reactivity is added to such a solution, an instantaneous color change occurs, but the color produced has been found to vary with the nature of the added base. For example, when diethylamine is added, the color of the secondary ammonium salt produced is "cornflower blue"; but if triethylamine is added, the solution becomes magenta. NBS studies using a large number of bases of diverse types revealed a characteristic pattern of behavior. Thus, the cornflower blue color produced by adding diethylamine is also obtained by adding other secondary aliphatic amines, while the magenta color is characteristic of tertiary amines. With primary amines the color becomes purple red, and a solution of a tetraalkylammonium salt of the indicator is blue, a "deeper" blue than that produced by secondary amines.

The effect of alcohol on these color reactions is interesting. When a very small quantity of alcohol is added to a hydrocarbon solution of a primary or secondary ammonium salt of the indicator, the color shifts to magenta. However, if the addition of alcohol is continued, the color shifts back toward blue and finally, after a relatively large volume of alcohol has been added, it becomes the same blue as a hydrocarbon solution of a tetraalkylammonium salt of the indicator. A small amount of alcohol does not affect the magenta color obtained by mixing the indicator with tertiary amines in organic solvents, but a large volume of alcohol changes the color to blue. Thus, alcohol appears to have a "leveling" effect, so that the same blue color results, whatever the base added to the indicator. Various other solvents, for example, acetone and acetonitrile, produce qualitatively the same effects as alcohol.

In practice, the colors exhibited by solutions of bases in bromophthalein magenta E are not limited to those described above. Thus, if an excess of the indicator is added to a tertiary amine in a hydrocarbon solvent, the magenta of the tertiary ammonium salt that is produced blends with the yellow of the unchanged portion of the indicator to give some tone of orange or red. Likewise, if unchanged indicator is mixed with the secondary ammonium salt (cornflower blue) produced by a secondary amine, a green tone will result. Practically any color in the visible spectrum can be obtained by varying the composition of the solvent and the character of the added base. However, all these color phenomena can be quite simply explained by applying the concept of hydrogen bonding. The application of similar reasoning to other acid-base reactions has thrown new

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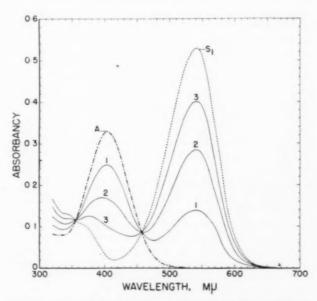


FIGURE 2. Spectral absorption curves showing the shift from yellow to magenta when increasing quantities of an organic base (di-o-tolylguanidine) are added to the indicator, bromophthalein magenta E. A: bromophthalein magenta E (2.5 × 10-6 mole per liter in benzene) without added base. Curves 1 to 3: approximately 7.3 × 10-6, 1.45 × 10-5 and 2.18 × 10-5 mole per liter of base present, respectively. S1 (limiting curve): approximately 6.25 × 10-4 mole per liter of base present. Series of absorption curves, such as the above, are used at the National Bureau of Standards in studying the reactions of indicators in organic liquids.

The Rare Earth Elements, -- A Neglected Phase of Inorganic Chemistry

• By Therald Moeller, Ph.D., (University of Wisconsin)
NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

In this important paper will be found the most recent information about the rare earths, a group of elements that have been so neglected that there are many misconceptions as to their availability, their properties, and their potential uses. Their chemistry is incomplete. Even some of their names are unfamiliar.

Dr. Moeller shows clearly that these elements can provide materials that will be of real value to both the theorist and the industrialist.

Here is one field of inorganic chemistry in which the number of problems for investigation is limitless.

In 1794, the chemist Gadolin isolated from a mineral obtained at Ytterby, Sweden, a new oxide (earth). Shortly thereafter, Ekeberg suggested that the oxide be called *yttria* and the mineral gadolinite. Both investigators believed the oxide to be that of a single element, and such a view was entertained until 1843, when Mosander separated from it three fractions of slightly differing characteristics.

In a period extending through about 1907, the original yttria was shown to be a mixture of compounds of no less than ten elements, including those we now call scandium and yttrium, and those of atomic numbers 64 through 71. In 1803, Klaproth isolated from another mineral an oxide which resembled Gadolin's yttria but differed somewhat from it. This oxide was soon termed ceria and the mineral cerite. In 1814, Berzelius established definitely the presence of a new element cerium in this material, but over a subsequent period extending into the early twentieth century, this seemingly simple oxide was resolved into compounds of some six elements ranging in atomic numbers from 57 through 63. Such were the beginnings of rare earth chemistry.

The rare earth elements embrace those of atomic numbers 57 through 71 and for practical purposes yttrium (number 39) as well, because of marked similarities in properties. These elements are characterized by general similarities which are more striking than those existing among any of the other elements, except perhaps the pair zirconium—hafnium, and the heaviest of the transuranium elements. Classically, their chemistry has been almost exclusively a chemistry of difficult and commonly tedious separations. The elements bear unfamiliar names and have seldom been considered in most discussions of inorganic chemistry.

As a result of the difficulties which have attended the recovery of these elements in high states of purities, many misconceptions have arisen relative to the rare earth group. Among these are views as to lack of availability, lack of any conceivable uses, lack of interesting or even important properties, and lack of any chemistry beyond the separations stage. Such views, although commonly held, reflect a lack of true understanding of these elements. The rare earth elements as a group are neither rare nor unavailable. Comparative data upon the relative abundances of these elements and many of those with which we are familiar, as shown in Table I, are enlightening.

With the recent discoveries of very sizable mineral deposits, the problem of supply is no longer critical, and the development of new and continuous techniques of separation give promise of providing many pure materials at less than prohibitive costs. The characteristics of the free metals, insofar as they are known, suggest the development of new and useful alloys. The characteristics of the compounds are vastly different from those of compounds of all other elements except those in the transuranic region. They provide excellent places for the testing of much chemical theory and have already been used to advantage in the optical and ceramic industries. True appreciation of the properties which this group of elements offers cannot help but lead to technical utilizations.

Comparative Properties of the Rare Earth Elements

The existence of this group of elements as a closely related series of materials is dependent upon electronic arrangements in atoms and derived ions. As electrons are added to produce elements of increasing atomic numbers, they invariably seek positions of lowest relative energy content. Among the lightest elements, this involves addition of these electrons to the outermost regions of the atom, i.e. to the highest available quantum levels. Such a situation pertains until scandium (atomic number 21) is reached, where it now becomes

TABLE I Relative Abundances in Crust of the Earth

Ele- ment	Grams/Metric Ton	Per	Cent	Ele- ment	Grams/Metric Ton		. (Cent
Se	5	5 x	10-4	В	3	3	×	10-4
Y	28.1	2.81 x	10-3	N	46.3	4.63	×	10-3
La	18.3	1.83 x	10-3	Co	23	2.3	×	
Ce	46.1	4.61 x	10-3	Ni	80	8.0	×	10-3
Pr	5.53	5.53 x	10-4	Cu	70	7.0	×	
Nd	23.9	2.39 x	10-3	As	5	5	X	10-1
Sm	6.47	6.47 x	10-4	Br	1.62	1.62	x	10-4
Eu	1.06	1.06 x	10-4	Cd	0.15	1.5	×	10-5
Gd	6.36	6.36 x	10-4	Sn	40	4.0	×	10-3
Th	0.91	9.1 x	10-5	Sb	1	1	×	
Dy	4.47	4.47 x	10-4	1	0.3	3	×	10-5
Ho	1.15	1.15 x	10-4	Hg	0.5(?)	5	×	10-5
Er		2.47 x	10-4	Pb	16	1.6	×	
Tm		2.0 x	10-5	Bi	0.2	2	×	10-5
Yb			10-4	Th	11.5	1.15	×	"
Lu			10-5	U	4	4	×	10-4

easier for the electron to add to an incompletely filled lower level (specifically the 3d). In the elements immediately following, this process continues, giving a series of elements—the first transition series—in which the outermost configuration remains essentially constant $(4s^2)$ and the differences lie in a level somewhat closer to the nucleus. After this level reaches capacity (=10 electrons), addition to higher levels continues as before. The same situation is encountered at yttrium (atomic number 39), and again at lanthanum (atomic number 57). After lanthanum, however, it becomes easier for added electrons to drop into the fourth quantum level where space for 14 electrons of the 4f type exists. It is this filling up of the 4f level which gives rise to the rare earth elements, as is shown in Table II.

The essential constancy of the outermost arrangement indicates clearly why these elements should resemble each other closely in their properties. It suggests also that in their compounds these elements might be expected to show a constant oxidation state. All of these elements do exhibit a +3 state of oxidation, and this state may be regarded as characteristic of the group. Slavish attention to this state of oxidation, however, has caused many to regard any other oxidation states as anomalous. Actually, a +4 state is wellknown for cerium, for praseodymium, and for terbium and a +2 state is characteristic of samarium, of europium, and of ytterbium. In these states of oxidation, the elements systematically attempt to achieve the very stable configurations of La(III) (no 4f electrons), Gd(III) (seven 4f electrons, or half-capacity of the level), and Lu(III) (fourteen 4f electrons, or capacity). The La(III) configuration is achieved by Ce(IV); the Gd(III) configuration by Eu(II) and Tb(IV); and the Lu(III) configuration by Yb(II). The much less stable Pr(IV) and Sm(II) may be regarded, respectively, as approaching the lanthanum and gadolinium arrangements.

Within the +3 state of oxidation, remarkable similarities in the solubilities, stabilities, and crystal structures of comparable compounds exist. Were it not for the operation of an additional factor, these tripositive ions would be indistinguishable from each other. However, the increase in nuclear charge in the rare earth series without compensating addition of electrons to higher and higher energy levels causes a general pull-

TABLE II Electronic and Size Characteristics

Element	Atomic Number	Ideali Electronic	conf		Empirical Radius of Ln+3 - A.
Se	21		3d1	4s2	0.83
Y	39		4d1	5×2	1.06
La	57		5d1	6s2	1.22
Ce	58	461	5d1	6a2	1.18
Pr	59	412	5d1	6s2	1.16
Nd	60	413	5d1	6s2	1.15
Pm	61	464	5d1	6a2	*
Sm	62	415	5d1	6s2	1.13
Eu	63	416	5d1.	6x2	1.13
Gd	64	417	5d1	6a2	1.11
Tb	65	418	5d1	6a2	1.09
Dy	66	419	5d1	6s-	1.07
Ho	67	4f10	5d1	6s2	1.05
Er	68	4611	5d1	6n2	1.04
Tm	69	4f12	5d1	6a2	1.04
Yb	70	4f13	5d1	6s2	1.00
Lu	71	4614	5d1	682	0.99

ing in of all the electrons toward the nucleus and a resultant decrease in size with increasing atomic number. This is the well-known lanthanide contraction and is illustrated in Table II.

Paralleling this change in size one can distinguish changes in the degree to which certain properties are exhibited—changes, for example, in solubilities, in tendency to form complex ions, in basicity characteristics, in compound stabilities, etc. These, of course, are the variations which make separations of these species possible. Examination of the size data in Table II indicates that the contraction effect becomes so pronounced that size drops to that of the yttrium ion and then below. As regards size, yttrium occupies a position between dysprosium and holmium.

It is reasonable to expect, then, marked similarities between the compounds of yttrium and the heavier rare earth elements in this region. Such similarities do, in fact, exist, and yttrium is always found in association in nature with this portion of the rare earth group. Indeed, the similarities are so striking that the heavier rare earth elements are often referred to as yttrium sub-group elements.

The rare earth elements themselves are lustrous. white metals which compare strikingly in their chemical reactivities with the alkaline earth metals. Thus, they are readily oxidized by oxygen, by water, by hydrogen ion, by sulfur, by the halogens, and even by hydrogen itself. They must, therefore, be preserved in inert atmospheres. When alloyed with iron, they give pyrophoric alloys of the mischmetal type. Suggested uses of certain of these metals in improving the qualities of castings are based upon their high chemical reactivities. The tripositive rare earth metal ions yield easily soluble nitrates, chlorides, bromides, iodides, perchlorates, bromates, and acetates; moderately soluble sulfates; and difficultly soluble oxides, hydroxides, fluorides, oxalates, carbonates, phosphates, etc. They form innumerable double nitrates, sulfates, etc., many of which can be readily crystallized.

Properties of the Tripositive Ions Related to Electronic Configurations

The almost unique electronic configurations of the tripositive rare earth ions impart to them unusual properties which are not duplicated among the common cations. Among these are magnetic properties, color and light absorption characteristics, and reluctance to form complex species.

Magnetic Properties.—Since the 4f arrangement consists of seven orbitals, it is possible to have up to seven unpaired electrons present in these ionic species. Since unpaired electrons are in general responsible for magnetic effects, it might be expected logically that many of the rare earth metal ions would be paramagnetic. This is indeed the case, only lanthanum $(4f^0)$ and lutetium $(4f^{14})$ ions (along with yttrium) being diamagnetic. With ions of the simple transition metals (e.g., Ti - Ni), magnetic moment is determined entirely by the number of unpaired electrons (actually d electrons) and reaches a maximum for those species containing the most such electrons. Data in Table III indicate,

TABLE III
Magnetic Characteristics of Tripositive Ions

Ion	Unpaired Electrons	Magnetic Moment, Bohr Magnetons
La-3		
Ce+3	1	2.39
Pr+3	2	3.47
Nd-3	3	3,62
Pm *3	4	2,83*
Sm+3	5	1.54
Eu+3	6	3,61
Gd+3	7	7.95
Td-3	4	9.6
Dy+3	5	10.5
Ho+3	4	10.5
Er.3	3	9.55
Tm+3	2	7.5
Yb*3	ī	4.4
Lu+3	ů.	

* Calculated

however, that such is not the case with the rare earth metal ions. The differences can be explained qualitatively in this fashion: Magnetic effects in chemical substances are due in general to the motions of unpaired electrons. These may involve either spin about an electron axis or orbital motion about a nucleus. With simple transition metal ions, the unpaired electrons are also the outermost electrons and are therefore so strongly influenced by adjacent species that their orbital effects become negligible in comparison with spin effects. With the rare earth metal ions, however, the unpaired 4f electrons are so screened from external influences that both spin and orbital motions are of importance. These effects do not vary in exactly the same fashion with the number of unpaired electrons, and the resultant of these effects gives the two maxima noted in Table III. Many of the rare earth species are particularly strongly paramagnetic.

Color and Absorption Spectra.—Certain of the tripositive rare earth metal ions are strikingly colored. It is of interest that a rather remarkable periodicity in color is noted among these species as shown in Table IV.

TABLE IV
Color Sequence of Tripositive Ions

Ion	Color	Ion
La+3 Ce+3 Pr+3 Nd+3 Pm+3 Sm+3 Eu+3	Colorless Colorless Greenish Reddish or pinkish (?) Yellowish Yellowish Colorless	Lu+3 Yb+3 Tm+3 Er+3 Ho+3 Dy+3 Tb+3
Gd-3	Coloriess	Gd+3

Inasmuch as color among the transition metal ions is again associated with the presence of unpaired electrons, it would not seem surprising to find color among the rare earth species. However, the situation is not quite so simple, as indicated, for example, by the fact that although the gadolinium ion has the maximum possible number of unpaired electrons (seven) it is colorless. A clue to the difference may be found in the more quantitative description of color in terms of absorption spectra. The absorption spectra of simple transition metal ions consist of a limited number of very broad and relatively intense absorption bands. The absorption spectra of the rare earth metal ions, however,

consist of numerous extremely sharp but not necessarily intense absorption bands distributed, depending upon the species, from the ultra-violet through the visible and into the near infra-red. Of the tripositive cations, only lanthanum, lutetium, and yttrium show no light absorptions.

The absorption bands of the rare earth metal ions are remarkable for their sharpness. Many of the peaks narrow down to a few Angstroms in width, and at low temperatures certain of the bands are under 1A in width. Such line-like absorption spectra are characteristic of no other cations except those in the transuranium region. It is of interest that these spectra characterize the ions whether in solution, in crystalline compounds, or in glasses. It is not surprising to find mixtures of rare earth oxides used in compounding glasses for accurate standardization filters, e.g. neodymium and praseodymium oxides to give didymium glass. Inasmuch as each species has its own characteristically placed absorption bands, it becomes possible, by choice of appropriate bands, to determine spectrophotometrically individual rare earth elements in com-

The origin of these characteristic spectra is again in the 4f level. It has been shown that the absorption bands result from electronic transitions within this level, transitions which might not normally occur but which become possible because of the electrical effects imposed by the anions adjacent to the cations. With the simple transition metal ions, it is the outermost electrons which cause absorption. These are also the electrons involved in the formation of complex species, causing the complexes of these elements to differ in color from the parent cations. With the rare earth metal ions, the origin of color is completely outside the realm of chemical reaction and compound formation, and color is, as a result, essentially unaffected by compound type.

Complex Formation.—The rare earth metal ions show a notable reluctance to form stable complex ions or coordination compounds. This is probably the result of the combined effects of unfavorable electronic arrangements for true covalent bonding and cation sizes too large to permit electrostatic attractions. The common complexing agents, e.g., ammonia, halide ions, cyanide ion, etc., are completely without effect. A few unstable ion-pair associations, e.g. CeCl+2, do exist in solution, but these cannot be isolated. The only complex species which have been truly characterized are those derived from chelating groups, i.e. groups which can attach simultaneously to a cation through two atoms. In all cases, complex stability increases with decreasing radius of the rare earth metal ion.

Citrate and tartrate form complex species which have been particularly useful in the new ion exchange methods for separating the rare earth elements. Ethylenediaminetetraacetic acid,

$$HOOCCH_2$$
 CH_2COOH $N-CH_2-CH_2-N$ CH_2COOH $(Continued on Page 109)$

Polyelectrolytes as Synthetic Soil Conditioners

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This is a story of KRILIUM, the new synthetic polyelectrolyte soil conditioner, first announced to the public late in 1951, and now widely used by gardeners to promote good soil structure.

Its long, thread-like molecules adsorb on silt and clay particles and bind them together with a network of threads that remain stable even when wet. This accounts for their improvement of soil structures and their ability to make heavy soils workable.

Krilium soil conditioner is still too expensive for soil treatment in large scale agriculture except where localized treatments are possible.

The importance of the physical properties of soil in agriculture was first described by Sir Humphry Davy in 1813, and by Schubler, who in 1833 reported the first technical investigation of soil physics. Little attention was given this branch of soil science however, since emphasis was placed primarily on the amount of nutrients in the soil. As a consequence the importance of soil physical conditions was rarely fully appreciated until the present century.

The physical characteristics of soil are determined largely by its texture and its structure. Texture usually refers to the relative proportions of sand, silt and clay particles present. Structure refers broadly to the arrangement of these primary particles into secondary clusters, or aggregates, which are relatively stable to water.

Soils that contain a high proportion of sand lack cohesion, have poor water-holding and nutrient-retention properties and may crust severely. They do not, however, become sticky or difficult to work and usually are sufficiently porous for good aeration. Soils that are high in clay, on the other hand, have better nutrient-retention properties but present problems of workability more often than do sandy soils. The clayey soils are inclined to hold too much water and hence become sticky and puddled, depending to a large extent upon their structure, or state of aggregation.

In a soil of poor structure, rainfall slakes the crumbs or soil aggregates and the particles pack tightly together. If considerable clay is present the soil becomes slippery and sticky when wet and very hard when dry. This results in a crusted surface. Seedlings have a difficult time emerging, partly because they must fight their way through a dense, compacted, crusted soil, and partly because they have difficulty obtaining air. In contrast a soil of good structure does not slake under the action of water. Moreover, porosity created by tillage, by plant roots, by burrowing animals and by freezing and thawing is more or less permanent. This porosity allows rainfall to penetrate the soil readily and allows excess water to drain away rapidly. The soil thus holds adequate water, but not at the expense of good aeration.

In soils of good natural structure the agents which bind soil particles into water-stable aggregates may be inorganic colloids, such as iron or aluminum hydroxide, or organic colloids. The constituents of soil organic matter are numerous and varied and the contribution of the various fractions to soil structure is not well defined.

Among the materials which add to the water-stability of soil aggregates are the fats and waxes from plant residues. These temporarily water-proof soil crumbs and decrease crumb breakdown in the presence of water. Similar organic materials such as rosin acids and oil have been used to stabilize soil for engineering purposes. Volatile silicones which water-proof soil crumbs were suggested for agricultural applications by Van Bavel. Our own experience has been that severe water-proofing is undesirable for agricultural soils because it reduces the rate of infiltration of water and the water-holding capacity of the soil and seems to interfere with normal plant growth.

Much importance has also been attached to the role

How DO ZINNIAS fare in hard-packed clay "problem" soil and in the same soil treated with Krilium soil conditioner? These soil profile photographs show how even this sturdy annual has difficulty in germination and emergence in compacted soil (at left). In treated soil (at right), which is loose and porous, zinnia plants push their way through the surface easily.



of lignoprotein complexes in soil structure. It may be that materials of this type bind soil particles together by a cementing action such as can be obtained with certain resin emulsions. These materials are not highly active as binding agents, and they seem to be somewhat irreversible as cements. In other words, aggregates broken down mechanically are not readily recemented. This form of soil organic matter undoubtedly contributes to the nutrient and water-holding properties of soil.

A third type of soil organic matter important in soil structure is the soluble gums. These are polysaccharides produced from plant residues by bacterial action and usually contain carboxyl groups. Shorey and Martin identified polyuronides in this fraction of soil organic matter in 1930 and a great deal of work since that time has established their importance in promoting good soil structure. While they are quite effective in binding soil in water-stable aggregates their action is short-lived since they are constantly being destroyed by soil micro-organisms.

Several years ago Monsanto Chemical Company became interested in the problem of soil structure and a screening program was undertaken for the purpose of finding chemicals which would promote good soil structure. Many types of organic and inorganic materials were tested in this program. It soon became apparent that one class of compounds, the synthetic polyelectrolytes, was particularly effective in increasing the water-stability of soil aggregates. These synthetic polyelectrolytes proved to be considerably better as soil conditioners than the naturally-occurring gums and were found to last much longer in the soil.

The soil conditioning properties of synthetic polyelectrolytes as soil conditioners were announced to the public in December, 1951. Krilium is the trade name for the products marketed by Monsanto Chemical Company as synthetic soil conditioners. To be effective as a soil conditioner of this type, the polymer must be water soluble at least to some extent, of high molecular weight, and contain a minimum of cross-linking. In other words the polymer molecules are long and threadlike. Physical chemical studies have indicated that they adsorb very tightly on soil particles, particularly on silt and clay particles, binding them together with a network of threads. Since the polymers are not leached from the soil with water, the soil aggregates remain bound together even when wet. This binding of soil particles into water-stable aggregates is the key to their action in improving soil structure.

Many polymers can be prepared which meet the requirements set forth above. The largest published list of different polymers tested as soil conditioners is in U. S. Patent 2,625,529, assigned to Monsanto. The two polymers which have received the most attention are the modified vinyl acetate-maleic acid compound and hydrolyzed polyacrylonitrile, which are sold under numerous trade names. A number of other polymers are under investigation.

The most obvious effect of soil conditioner treatment of silt and clay soils is a pronounced improvement in workability. Heavy clay soils can be made loose and friable, and their stickiness reduced or eliminated. The soil is given the spongy properties shown by natural soils of excellent structure. This effect is particularly apparent in the spring when untreated soil is wet and soggy, but treated soil is quite spongy and workable.

The moisture relationships are improved remarkably when a soil of poor structure is treated with a polyelectrolyte, such as Krilium soil conditioner. Since the

aggregates do not slake badly, the porosity created by tillage is retained and the soil does not crust badly. Rainfall enters the soil more rapidly and seeps downward through the large pores. Excess water drains readily and conditions of good aeration are rapidly reëstablished.

Still another effect of conditioner treatment is the fact that more moisture is held against loss by evaporation in treated soil than in untreated soil of poor structure. Such moisture retention is a property of good structure. In a slaked soil there are many continuous capillary pores leading into the surface through which moisture moves only to be lost by evaporation. Also water vapor is lost through the large cracks that open up when the slaked soil dries out. In an aggregated soil, on the other hand, there are fewer continuous capillary pores and hence less moisture moves to the surface. The surface of conditioner-treated soil dries out rapidly because moisture does not move up from below; and the dry surface produces a mulching effect.

The effect of conditioner treatment upon plant growth is largely an indirect one. These polyelectrolytes are not fertilizers,

Tests by 23 state highway departments are now in progress to determine the effectiveness of Krilium soil conditioner in controlling erosion of highway slopes. The new material, which has proved useful in controlling wind and rain erosion of soil in numerous studies conducted by Monsanto and its many technical cooperators, is being tested on a wide variety of soils found near highways in many states, and in other projects in which erosion control is important.



although they may enable the plant to use added fertilizer more efficiently. In soils where natural structure is poor the conditioner improves aeration, and encourages root growth and nutrient absorption. The air, nutrients, and water which a plant needs from soil can all be available to plants in the good structure created by a proper treatment with a soil conditioner.

The conditions present in the soil at the time a treatment is made are very important in determining how effective the treatment will be. The conditioner does not create structure; it tends to stabilize the structure present at the time of treatment. The mois-

TABLE I

Distribution of Water-Stable Aggregate Sizes at Various
Concentrations of Vinyl Acetate-Maleic Acid Copolymer
as measured by sieving under water.

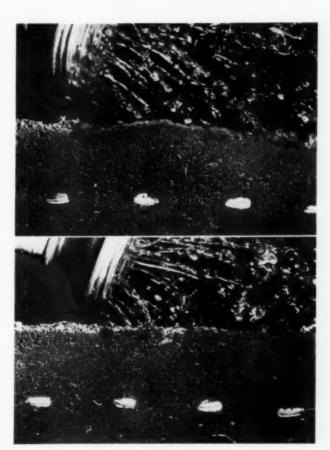
Concentra- tion of Polymer	Wate	Total		
in Soil, %	>0.84 mm.	0.84-0.42 mm.	0.42-0.25 mm.	
0.0	0.0	0.0	0.5	0.5
0.002	0.8	1.0	2.2	4.0
0.005	1.3	4.0	8.5	13.8
0.01	7.5	20.8	21.2	49.7
0.02	28.5	31.0	10.2	69.7
0.05	63.5	14.5	5.6	83.6
0.10	73.3	10.7	5.0	89.0

ture content at which the soil is treated and the amount of mechanical working given the soil affect the distribution of the polymer and also the amount of water-stable aggregates formed by a treatment. In field use the conditioner adds to the natural level of aggregation. Since in use the polymer tends to stabilize the structure present at the time treatment is made, best results are obtained when the soil is at an optimum moisture content for working because the best structure is produced under these conditions.

Other factors which affect the degree of aggregation obtained with conditioner treatment are soil variables such as texture, pH and electrolyte content. As yet the response of a given soil can be determined only by a trial treatment; in general silty loams seem to give a good response. Clay soils give the most dramatic improvement in workability although higher rates of application are required for this type soil.

The increase in the water-stable aggregates obtained by a conditioner treatment also depends upon the rate of application. Table I shows the size distribution of water-stable aggregates which were prepared by treating pulverized Miami silt loam with various amounts of the copolymer of vinyl acetate with maleic acid. The soil conditioner was added in sufficient water to bring the soil to 30% moisture level. Crumbs were prepared by pressing the moist soil through a sieve with 4-mm. openings. Crumbs prepared with water containing no polyelectrolyte served as a control. It can be seen that an increase in the rate of treatment gives more water-stable aggregates larger than 0.25 mm. and also a larger proportion of large aggregates.

How long will treatment with Krilium soil conditioner last? is a question often asked. The answer appears to depend on several factors: the rate at which it is



WHAT HAPPENS WHEN water strikes untreated clay "problem" soil and the same soil treated with Krilium? In the upper photo the displacement and battering down of the soil are clearly shown. Below, treated soil remains in position and absorbs water readily. Surface runoff of water is greatly reduced; infiltration and percolation of water are improved. A special photographic technique was used to "stop" the action of water drops.

applied, the efficiency of the treatment, the soil itself and the tillage and attention given the soil. Rainfall and freezing and thawing are factors which may lead to mechanical breakdown in outdoor treatments over long periods of time. The moisture content at time of tillage is an important factor in the maintenance of good structure in treated soil, as well as in any other soil of good structure, because soil which is too wet or too dry when tilled has its structure damaged. Microbiological breakdown of the polymers is believed to be very slow and leaching of the polymer is negligible. With good care, conditioner-treated soil retains most of its improvement after three and one-half years.

At present, soil conditioners are too costly for treating acres of soil to plow depth for general agriculture. The treatment is, however, not too expensive for use in lawns, flower beds, home gardens, greenhouses, tobacco seed beds and baseball diamonds. Commercial vegetable growers have found soil conditioners to be advantageous in hot frames and flats where seedlings flourish in treated soil prior to transplanting. In such applications, all of the soil can be treated to the desired depth for improved workability and aeration. Shallow treat-

(Continued on Page 102)

Detection and Evaluation Of Hearing Impairments

• Thomas J. LePine

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Upwards of two million school children in the United States suffer various degrees of hearing loss. Probably more than half the defects might be corrected or alleviated if they could be discovered early enough.

New York State maintains in its public schools a highly successful conservation of hearing program that could well be a pattern for other states. It is designed to discover and to provide for the medical and educational needs of pupils with impaired hearing.

This is an interesting account of how the program operates.

A conservation of hearing program is mandated in the schools of New York State. It is considered an integral part of a total health service program. The purpose of this program includes the discovery of all children with hearing impairments and the assurance of proper medical and educational follow-up services to such children.

The need for such a program is evident when we consider the results of surveys which report that in any given state or local community approximately 1.5 per cent, or 1 in 66 school age children may be found to be hard-of-hearing or deaf to the extent that special educational services may be needed. It is further estimated by several authorities that throughout the United States there are approximately 1,500,000 to 2,000,000 school children with various degrees of hearing loss.

Hearing Acuity Tests

The discovery of hearing loss is dependent upon the alertness of parents, school doctors and school person-

nel. In our schools annualhearing tests are given to children by means of audiometers NORMAL o which have been approved by the Council on Physical Medicine and Rehabilitation of the American Medical Association. Audiometers most commonly used to do the testing are the "phonograph" or "speech" type and the "pure-tone" or "discrete fredetection of hearing impairments through screening tests in which up to 40 children participate simultaneously. Pure-tone audiometers can also be used for preliminary screening tests, however, their most important application is in the detailed analysis not only of the degree but of the particular characteristics of individual hearing impairments.

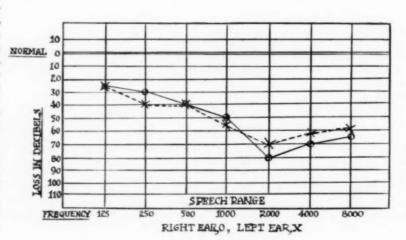
quency" type. Phono-group audiometers are used in the

Phono-audiometers consist of a phonograph mechanism which feeds into a group of headphones. They make use of disc recordings of spoken numbers that gradually diminish in sound intensity. Children being tested are instructed to write down on a printed form the numbers they hear. As the intensity of the numbers becomes weaker and weaker, hearing impairments are detected. When the test is completed, the children's papers are checked and those who fail are re-tested with the same instrument. Children who fail the re-test are given a full threshold acuity test using a pure-tone audiometer.

Pure-tone audiometers are electronic devices in which pure tones are generated. The frequency and intensity of the tones are varied by means of control dials. Frequencies obtainable on most audiometers range from 125 to 10,000 cycles. The sound intensity is given from a level, so low that it is likely to be inaudible to a person with normal hearing, to an upper limit which is about as loud as the average person can comfortably stand. This instrument may be used to obtain a complete graph or audiogram of a child's hearing, or as a screening device employing the "sweep check" technic. When it is used for screening purposes, the sound intensity control is set at a level which makes the sound clearly audible to persons of normal hearing, but not audible to those who have a significant hearing impairment. The frequency control dial is then rotated through the various frequency ranges and the child's

response is noted. If a child fails to respond to two or more frequencies at an intensity of 10 decibels, he should be given a full threshold acuity test.

When a child is discovered through the phono-group or sweep check screening tests to have a hearing loss, a more thorough evaluation of the impairment is secured through the



use of the pure-tone audiometer. When this instrument is employed the procedure is to measure the lowest sound intensity that the child can hear at each of the various frequencies distributed throughout the full range of the instrument. In all instances, this audiometer is used to test children individually.

The Audiogram

Measurements obtained from the pure-tone audiometer present a permanent record in graphic form, called an audiogram. The accompanying audiogram graphically shows the level of hearing at each frequency. Measurement points shown in the form of circles connected by a straight line are of the right ear. Left ear measurements are indicated by "X's" connected by a dotted line.

For a person with average normal hearing, the two lines shown on the audiogram would coincide approximately with the double horizontal lines at the zero level. Audiogram lines extending below this level show impairments. The extent of the impairment is read directly in decibels from the scale at the left of the chart. Decibels are used to measure hearing loss for such units closely approximate a ratio of sound intensities which can be detected by the ear as slight differences in loudness.

Types of Deafness

An analysis of audiometric curves may assist an otologist (ear specialist) to decide which type of hearing impairment is present. The two fundamental types of deafness are "conduction" deafness and "nerve" or "perceptive" deafness.

When a conductive type loss is present, the hearing difficulty is located in the outer or middle ear and is generally caused by some sort of blockage. The most common causes of blockages are impacted wax in the ear canal, scars of old healed perforations of the ear drum which restrict its movements, and adhesions of scar tissue on the tiny bones of the middle ear. Normal movement of these bones may also be restricted by the new bony growth of otosclerosis.

When a perceptive or nerve type impairment is present, the sound probably gets to the inner ear; however, a portion of the ear mechanism is not functioning properly. This type of deafness generally implies a degeneration of the elements of the sense organ or the auditory nerve and can rarely be improved by medical treatment.

Educational Adjustment

Recommendations concerning educational adjustments may be made when information supplied by the audiogram is supplemented by a thorough examination of the ears, nose and throat and a comprehensive case history of the individual. Often times, it is learned that a child has a permanent hearing loss; therefore, means of minimizing the resulting handicap must be considered. These considerations are based on the type and degree of impairment, its effect on the child's general behavior and his ability to communicate with others. Case study and educational follow-up procedures should be gov-

erned by the findings of the otologist in conjunction with the advice of the school administrator, school nurse-teacher, guidance counselor, attendance workers, psychologists and other personnel who constitute the school team.

Audiometric screening will reveal many children with hearing loss under 20 decibels that is related to acute or chronic upper respiratory conditions. These infections generally can be treated successfully; however; it is important to discover and treat such conditions early for they may progress to a point where they may be irremediable. Children with such loss need not only prompt medical attention, but also careful supervision by both teacher and parent while medical treatment is being carried out. Classroom teachers may have to change the child's classroom seat so that he can work to best advantage. They should observe the manner in which he participates in group discussion and keep a watchful eye on his progress. It might also be advisable to offer the child some speech reading training as a precautionary measure.

If a child has a loss of hearing which does not exceed 35 decibels it may suffice to teach him speech reading and provide suitable seating for him in the regular classroom. Authorities have stated that children with an average hearing loss of 35 decibels or more should be given a carefully selected hearing aid and should be trained in its use. Speech training or speech correction may also be needed by those children whose loss interferes with the development or retaining of certain speech sounds.

Children with hearing loss ranging from 55-75 decibels in the speech range, in the better ear, present a complex educational problem for they must be taught to communicate by specialized technics designed to fulfill the needs of their total adjustment. These children generally adjust more readily in special classes for the hard of hearing or in schools for the deaf. Children who attend special classes in public schools usually can participate in regular classroom activities to some extent.

Deaf children with unusual abilities and advantages may be able to fit into regular classes, however, they are usually considered the exception and not the rule. It is the consensus that children with profound hearing loss should receive their education in a special day or residential school for the deaf when it is learned that they are not progressing favorably in the regular classroom and every possible measure of case study has been investigated to ascertain any possible procedure that might be helpful to the child.

Many known cases of hearing loss in adults have their origin in pathological conditions present in childhood. It is further believed that from 50 to 60 per cent of all hearing impairments among children may be corrected or alleviated if they are discovered early enough. Conservation of hearing programs which insure early detection of hearing loss and efficient medicaleducational follow-up procedures will assist hard-of-hearing children to assume their place satisfactorily in the society of which they are an integral part.

The Work of the Committee on Diagnostic Reading Tests, Incorporated

• By The Committee

FRANCES ORALIND TRIGGS, chairman; ROBERT M. BEAR; RALPH BEDELL; JOHN V. McQUITTY; GEORGE D. SPACHE; ARTHUR E. TRAXLER; FREDERICK L. WESTOVER, former members of the Committee; IVAN A. BOOKER; DANIEL D. FEDER; CONSTANCE M. McCULLOUGH; A. EASON MONROE.

This article reports the work being done by an interested group of workers to help schools and colleges individualize their programs of reading instruction.

The members of this Committee believe that most children by normal classroom processes can be taught to read effectively. Much of the remedial work now given in our schools could be eliminated. Every teacher should teach reading.

Teachers must first of all be able to recognize the reading level of students. The battery of reading tests constructed by the Committee has proved to be of value. They are being improved steadily by continued research and ways of using them in the teaching of reading are being stressed in committee publications.

The Committee on Diagnostic Reading Tests, Inc., is a non-profit educational organization, incorporated, for the protection of its funds, as a membership corporation in the State of New York. Its members are elected by the Committee itself on a rotating policy defined by its by-laws and articles of incorporation. The Committee, recognizing the lag which exists between what research has shown concerning the teaching of reading and teaching practice, devotes its resources and energies to activities that help schools and colleges to individualize their programs of reading instruction. The Committee concerns itself with the needs of each student in order that he may use reading more efficiently as a tool for personal development and enjoyment, and for discharging his social responsibility.

The work of the Committee started in 1943 with the aid of a grant from the Blue Hill Foundation but it was not until 1945 that it was formally organized. In 1947 it was incorporated. In order to determine the procedures by which the Committee could best meet its objectives, it canvassed the opinions of many teachers of reading and professional workers in the field. The results of that survey of opinion made it clear that one of the greatest stumbling blocks to efficient teaching of reading was the inability of teachers to recognize the reading level of students and thus to apply the cardinal principle of all teaching, namely, to start where students are and proceed to a well-defined objective. The Committee therefore decided to construct measuring instruments for the skills already defined as the major areas of reading instruction. Teachers would then have tests with which to measure the essential reading skills and the test scores could be used directly as guides to both group and individual instruction in reading.

The Committee believes that through the normal processes of classroom teaching most children could be taught to read efficiently, if a program of this kind ever became effective. A large part of the "remedial" work which has developed widely in our schools could thus be eliminated, because instruction would be individualized to the extent necessary to meet the needs of most students. Many who now become retarded readers would never become "remedial" cases. The Committee proceeded, therefore, to develop a battery of reading tests which are scored in areas of instruction in reading rather than in terms of "pure factors" which might ultimately be set up by application of advanced techniques in test construction.

The test basic to the whole battery is a Survey Test which may properly be administered to all students in any school, grades seven through college freshman year*. It is scored in three areas of instruction: rate of reading with satisfactory comprehension of story-type material; general vocabulary; and the ability to comprehend textbook or work-type material. The test is planned for administration in one classroom period. It is adapted for use with answer sheets which may be either hand or machine scored, or pupils may record their answers in the test booklet directly. There are eight comparable forms of this test.

A series of Diagnostic Reading Tests, constructed for easy classroom administration, was also developed in all three areas for which the Survey Test is scored. These are: the Vocabulary Test, which measures technical vocabulary in the fields of literature, science, social studies, and mathematics; the Rates of Reading Tests, which measure the flexibility with which students read when faced with differing objectives in reading, and their rates of reading science and social studies material; and the Comprehension Tests which measure the ability of the student to comprehend textbook type material both when he reads it himself and when it is read to him. The Committee also constructed diagnostic tests of word recognition skills, both oral and silent because it is recognized that word recognition skills are basic to the teaching of other reading skills. All of these tests have as many comparable forms as seemed necessary for the use to which they were to be put. All the tests as well as all other publications of the Committee are the product of the joint effort of its members.

The Committee has utilized the best standards of test construction applicable to its work. It has actively developed new norms as soon as the data have been available. The validity and reliability of each test

^{*}In the spring of 1952 the Survey Test: Lower Level (Grades 4-6) was added to the battery. It measures word recognition, comprehension, vocabulary, and rate of reading story type material.

have been extensively studied. Moreover, the Committee is engaged in a continuous program of research both to improve the tests it publishes and to make the results of its tests more effective in instruction.

All materials sold by the Committee follow a price schedule formulated by the auditors on the basis of production costs. No member of the Committee receives any compensation for his work. Therefore, only clerical, physical overhead and production costs are included in these cost figures.

The activities of the Committee in carrying out these policies over the seven years of its existence will now be outlined.

In the fall of 1947 the Committee made available two forms of the Survey Test (A and B) and during that academic year produced all of the tests in the diagnostic battery. This battery consists of Section I: Vocabulary; Section II: Comprehension, Part 1, Silent, Part 2, Auditory; Section III: Rates of Reading, Part 1, General, Part 2, Social Studies, Part 3, Science; Section IV: Word Recognition, Part 1, Oral, Part 2, Silent.

In the fall of 1948, forms C and D of the Survey Test—comparable to Forms A and B—were published. An extensive norm program and study of the comparability of forms of the Survey Test was conducted. This work carried over through 1949.

In the fall of 1950, Forms E, F, G and H of the Survey Test were published. At the same time another extensive program to establish norms was undertaken as well as a study of the comparability of the new forms of the Survey Test in relationship to forms already published.

In the spring and summer of 1950, new normative data and other minor changes were incorporated into the directions for administering some of the tests in the battery. In the fall of 1950, revisions of the directions for administering the following sections were published:

Directions for administering the Survey Section. Tentative revision.

Directions for administering Section II: Comprehension, Part 1, Silent and Part 2, Auditory.

Directions for administering Section III: Rates of Reading, Part 1, General, Part 2, Science, and Part 3, Social Studies.

New norms were developed during 1950 for Section IV, Word Attack, Part 2, Silent, and made available in mimeographed form.

The following studies and articles were either presented at professional meetings or published in the

- Booker, Ivan A., "Shall We Correct Neglect of Reading Skills?" Peabody Journal of Education, Vol. XXV, May, 1948, pp. 264-267.
- 2. Cummings, D. M., "An Examination of the Oral Diagnostic Reading Test, Form A." Unpublished Bachelor of Arts Degree Thesis. Hanover, N. H.: Dartmouth College, Department of Psychology, 1949.
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- Triggs, Frances Oralind, "Newer Trends in Remedial Reading," The Reading Teacher, Vol. 5, No. 4, Feb., 25, 1952, pp. 4-5.
- Triggs, Frances Oralind, "Report on Measurement of Reading Skills and Reading Therapy,"
 Proceedings and Papers of the Twelfth International Congress of Psychology, Edinburgh, Scotland, 1948, p. 118.

The Committee has tried at least once a year to give all users of its tests and others interested in the betterment of reading instruction, some service over and beyond the regular Committee publications. In the spring of 1949, the Committee distributed to schools which had evidenced an interest in the tests, an article by one of its members which reviewed reading tests and how to use them*. In September, 1949, it prepared "Questions on Reading," an article in the Clearing House. It then had this article reprinted and distributed 50,000 single copies without charge to schools all over the country. The response to "Questions on Reading" was favorable and those who wrote in about it asked many more questions. Therefore, in the spring of 1950, "Questions on Reading II" was prepared in

^{*}Traxler, Arthur E., "Measurement in the Field of Reading," The English Journal, XXXVIII, No. 3, March 1949, pp. 143-149.

order to serve more completely the needs of teachers of reading. Again the Committee distributed 50,000 single copies of this report. These publications are now embodied in a bulletin* on use of the tests.

The Committee keeps in close touch with users of the tests in order to find out how the tests are actually being used and how instruction is affected. The tests were originally based on data obtained from a survey of practices in reading. Twice since then the Committee has surveyed reading programs. In all cases, the forms on which the data were gathered were constructed not only to obtain data efficiently, but also to suggest practices which might be used. In order to fill in the forms adequately, the person reporting had to make a careful evaluation of the program in terms of certain criteria not necessarily universally applicable but which might be adapted to individual programs. In all of these cases many copies of the survey forms were requested by directors of the programs to use as the basis of discussing criteria for further development of their reading programs.

Beginning in the summer of 1950, the Committee cosponsored with the University of Maryland its first annual Work-Conference in Reading for persons with experience in the teaching of reading at any level of instruction, grade or college, or experience with tests and their administration. Each student, before being admitted, was required to define and outline what he wanted to gain from the Conference and only persons with well-defined objectives were admitted. The Committee plans to sponsor similar conferences each year.

In 1949 the Committee had what it considered an unusually good opportunity to introduce the materials to a large number of teachers who either through lack of knowledge concerning them or lack of ability to pay for them, probably would not otherwise be able to use the Diagnostic Reading Tests. The Reader's Digest Educational Service, Incorporated, a non-profit educational organization maintained by the Reader's Digest, wanted a standardized test to be used in conjunction with the Educational Edition of the Reader's Digest. This is the edition sold to schools and used in classroom instruction. It was possible to publish the tests in the educational edition in such a way that they could be torn out by the teachers before the children received the magazine itself. Careful instructions for administering the test, special instructions for interpreting the scores, and norms were made available through the Teacher's Guide which accompanies orders for the Educational Edition of the magazine. The fact that confidential tests were included in the shipment was made known by a special marking on the outside of each package. Also, it was planned that no teacher would receive the issues for the months in which the tests were included unless she previously stated that she would follow the plan set up to guard their confidential nature.

Forms A and B were used by the Reader's Digest Educational Service, Inc., in the fall and spring of 1949-50, and Forms C and D were used in the fall and spring of 1950-51, respectively.

*Diagnostic Reading Tests: Their Interpretation and Use in the Teaching of Reading.

All correspondence and questions concerning the use of the tests and the interpretation of their results were forwarded to the Committee by the Reader's Digest Educational Service, Inc., for personal answer by the Committee. Thus the Committee was in a position to give direct help to teachers not only in testing but in using the test results.

The Committee was aware that not every teacher would guard the test results according to the plan. Some misuse of the tests was anticipated, but the dangers of misuse seemed to be a calculated risk less important than the advantages to be secured from serving so large a group of teachers and their students. The Committee was able to compensate for this risk, in part, by developing four additional comparable forms of the Survey Test, Forms E, F, G, and H. Forms G and H will never be released to users through any other than the usual manner of distributing standardized tests. In this manner the Committee has tried to meet the possible objection of users that some carelessness may have resulted through wide distribution of the earlier forms thus possibly affecting the validity of norms and other evaluative data.

As a matter of fact the wide use of the tests in the Reader's Digest educational program allowed the Committee to check the representiveness of its norms and to expand them where advantageous. The results of this testing enabled the Committee to set up regional norms for the Survey Test.

The work of the Committee is reported in four publications other than test booklets.

The first is a separate booklet for each test containing directions for administering and the information which teachers will find useful in choosing, and scoring the tests. These booklets are entitled *Directions for Administering*.

The second is a norm book for the total battery of tests. Each norm group is carefully described and titled in order that the most appropriate one may be easily selected. This publication is entitled *Diagnostic Reading Test: Norms*.

The third publication is the manual on uses of the tests which discusses fully the interpretation of scores on each section and part of the test battery, both in terms of test results and in terms of the reading instruction which should follow the interpretations of various types of scores. This publication is called Diagnostic Reading Tests: Their Interpretation and Use in the Teaching of Reading.

The fourth is a pamphlet which brings together all information concerning the construction of the tests in order that those who are interested in test construction, as such, will have at hand as complete data as it is possible to give in summary form. This publication is entitled *Diagnostic Reading Tests*: A History of Their Construction and Validation. ●

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If science teaching is to be effective, it must display the creative imagination at work quite as vividly as does the best kind of teaching in literature and philosophy.

—I. Bernard Cohen

Harvard University

NEW BOOKS

Principles of Plant Physiology

 By James Bonner and Arthur W. Galston. San Francisco. W. H. Freeman & Co. 1952. Pp. 509. \$5.50.

This textbook treats of the functions of plants. It is divided into three parts: Part I, Nutrition, seven chapters; Part II, Metabolism, six chapters; Part III, Growth and Development, seven chapters. Each of the twenty chapters is followed by a set of questions and a bibliography.

The authors relate the material in the text to both physics and chemistry whenever the opportunity offers. They direct the illustrative material and questions toward practical applications, often agriculture. Only able and well trained men could present these relationships in the clear and simple style used in the text. The success in presentation is due in part to the frequent and skillful choice of well-understood, non-technical words; and in part to the substitution of three dimensional "animated" diagrams for graphs and tables, or for long, detailed descriptions.

In cases where contradictory theories regarding a given function exist, the authors have selected and described in detail only the most acceptable one. If other theories are mentioned they are treated briefly, and evaluated. For example, the "pressure-flow" theory is described to account for the movement of materials in the phloem; only two other theories are mentioned, and these are declared untenable because of lack of conclusive evidence.

In the opinion of this reviewer the authors have admirably achieved their aim of writing an elementary textbook that presents the functions of plants in a manner "sufficiently clear and decisive to permit the student to visualize and grasp clearly . . . basic principles involved."

Helena A. Miller, Ph.D. Department of Biology Duquesne University

The Scientific Adventure

• By HERBERT DINGLE. New York: Philosophical Library. 1953. Pp. vi + 372.

This book is a collection of lectures and addresses on the history and philosophy of science, delivered by this London Professor at various occasions between 1937 and 1950, most of which have been published before in learned periodicals. The collection consists of an introductory essay on The Missing Factor in Science, eight lectures on the history of science, and eleven on the philosophy of science. The historical section of the book is mostly concerned with astronomy and related studies. In general, it makes excellent reading, although



at times certain misconceptions make a brief appearance. For example, there seems to be confusion in the mind of the author about the nature of metaphysics on pp. 49ff. and 80ff.; the Church did not and does not need the Ptolemaic universe to maintain its dogmas of "creation and judgment" (p. 76); a little study of theology would have shown the author that the mystery of the triune God cannot be compared to the problem of waves or particles with respect to electrons (p. 80).

In the second part of the book the author gives an able explanation of his philosophical views, which in the main are positivistic and idealistic.

Henry J. Koren, C.S.Sp., S.T.D. Department of Philosophy Duquesne University

Introductory Mycology

 By C. J. ALEXOPOULOS. New York: John Wiley & Sons. 1952. Pp. 482, 187 figs. \$7.00.

The need of a satisfactory text-book for an introductory, one semester course in mycology has been fulfilled by this book. The problem of including sufficient detail without permitting details to become unwieldy and cumbersome has been solved, while an extensive bibliography after each chapter challenges the teacher or student of the fungi who desires to seek additional information. This text is especially noteworthy because of its readability.

The author has added immeasurably to the stature of his text by including an abundance of clear photographs and drawings. The inclusion of several illustrated life cycles is likewise an outstanding feature. The presence of an extensive mycological glossary with derivations of the terms will be of value to all students. An unusual feature of this text is the inclusion of chapters on the bacteria, actinomycetes, and the usually neglected Fungi Imperfecti.

Professor Alexopoulos has treated the fungi according to the system usually accepted by contemporary mycologists. The *Phycomycetes* are arranged in three series, the *Uniflagellatae*, *Biflagellatae* and *Aplanatae*, as advocated by Sparrow, Bessey and Karling. The *Ascomycetes* are divided into two subclasses, the *Protoascomycetes* and the *Euascomycetes*, with the latter being subdivided into *Plectomycetes*, *Pyrenomycetes* and *Discomycetes*. The traditional subdivision of the *Basidiomycetes* into *Hemibasidiomycetes* and *Holobasidiomycetes* has been adhered to.

A text such as this has long been needed in mycology. It will be of value to both beginning and advanced students.

Adrian W. Poitras, Ph.D. Department of Biology Duquesne University

Waves and Tides

By R. C. H. RUSSELL, M.A., and COM-MANDER D. MACMILLAN. New York: Philo-sophical Library. 1953. Pp. 348. \$6.00.

Sir Isaac Newton was the first to discover the fundamental mechanism of tides. But long before his time, and ever since, waves and tides have been studied for many practical reasons, especially because of their effect on man-made structures both floating and fixed, their transportation of materials, and their influence on navigation and the weather. Modern oceanographic research has provided answers to many problems once

thought to be insoluble.

Waves and tides are both alike and different, and this book considers them under one cover, a departure from custom. There are really two books: the first written by Mr. Russell is concerned with Waves; the second, by Commander Macmillan, deals with Tides. Both authors write well and with so little unnecessary use of technical terms that, except in a few sections, the book can be read with profit and pleasure by persons not trained in science or mathematics. The reader learns how waves are generated, how they are measured, how deep-water waves change as they near the shore, and how great damage may be caused. He is told about tidal theories, about the necessity for the navigator to understand tides, and how continuous local observations are made throughout the world. Space is devoted to tide-predicting machines and to the utilization of tidal energy. Over 100 line drawings and 17 excellent photographs clarify the text and add to the H.C.M.interest.



Modern Asia Explained

• By W. R. McAULIFFE. New York: Philosophical Library. 1952. Pp. vIII + 163.

Attempting to "explain" modern Asia in a book of 158 pages is an ambitious project that can of course be realized only in part. The writer appreciates the diffi-culties. In the Preface he states:

"This book is a modest attempt to give in simple language some account of the development and aspirations of the Asiatic states which have recently freed themselves, or been freed, from Western colonization and economic penetration. Some effort has been made to sketch the historical, social, and religious backgrounds to this development. In so short a compass, and in such simple terms, the task has not been easy, and I am fully conscious of the limitations and deficiencies which have arisen from condensation and simplification.'

The history, development, and aspirations of certain Asian states and their economic and religious backgrounds are discussed. How completely may be judged by the fact that but four pages are devoted to Japan, four to Israel, five pages to Turkey, and one each to Formosa and Korea.

H. C. M.



Synthetic Soil Conditioners

(Continued from Page 95)

ments for the control of crusting and erosion are feasible for general agriculture and truck farming, particularly where only a band over the row is treated to enable the seedling to emerge or for holding seed and soil in place on freshly seeded lawns and roadside berms. Band treatments down the row to 2- to 6-inch depths also greatly reduce the amount of conditioner required. Perhaps even treating restricted soil areas adjacent to the plants themselves will prove practical.

In addition to the applications mentioned above, synthetic soil conditioners have proved to be excellent research tools. They enable the soil scientist to control soil structure without a simultaneous change in nutrient status of the soil, such as occurs in manure treatments.

Synthetic soil conditioners are in their infancy and there remains much to learn about the most effective ways of making and using them, and about the response of various soils and various plants. There is no doubt, however, that they have a useful function to perform and that many improvements will be forthcoming. •

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Chelating Agents

(Continued from Page 81)

bearing compound since it is tied up in this non-ionic form.

It is important to point out that the complexes formed with these chelating agents become less stable as the pH is reduced and show maximum stability at high pH's. This factor should be remembered when considering applications for these compounds. Furthermore, the chelating power with ions of heavy metals such as copper, cadmium, tin, zinc, lead, manganese, nickel, cobalt and other divalent metals is stronger than with the alkaline earths such as calcium, magnesium, barium and strontium. In most cases, the higher the valence of the metal ion the greater is its tendency towards chelation. This is by no means a definite rule, since certain conditions may alter this, but chelate complexes are also formed with such trivalent metal ions as Al⁺⁺⁺, Fe⁺⁺⁺, and Cr⁺⁺⁺.

In general, it may be stated that most metals are chelated above a pH of 5, while heavy metals may be chelated at somewhat lower values of pH. It is well to again point out that the higher the pH the greater the chelating power.

Comparing the reaction of the Ca++ with Graham's Salt and the reaction of this same ion with the sodium salt of EDTA, we arrive at the following:

where
$$\begin{array}{c} \text{Ca}^{++} + \text{Na}_4 \text{Y} \rightarrow \text{Na}_2(\text{Ca}\text{Y}) + 2 \text{Na}^+ \\ -000 \cdot \text{CH}_2 & \text{CH}_2\text{COO}^- \\ \text{Y} = & \text{NCH}_2\text{CH}_2\text{N} \\ -000 \cdot \text{CH}_2 & \text{CH}_2\text{COO}^- \end{array}$$

The brackets in the formula for the calcium complex indicate that the calcium is bound up in a non-ionic complex with the sodium salt of EDTA. As in the process of sequestration, the calcium ion loses its chemical or ionic identity in this process of chelation.

A general reaction to illustrate the chelation of any metal ion capable of being chelated is shown in the following reaction:

ONE HUNDRED AND FOUR

The exact structures of the calcium chelate complex and of other metal complexes have been investigated. Suffice it to say that it is not a definite structure. For the benefit of those interested, the structure has been postulated to be one of the three forms indicated below, form (3) being the most probable:

(1) Coordinated With All Four Carboxyl Groups and Two Nitrogens

(2) Coordinated With Only the Four Carboxyl Groups and No Nitrogen Atoms

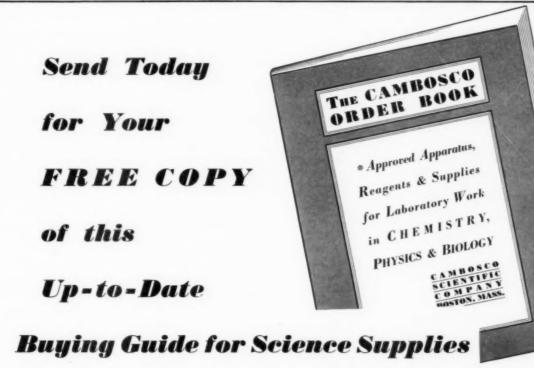
(3) Coordinated With Two Nitrogens and Two Negative Carboxyls

As stated, other structures are possible, but experimental evidence shows the preceding to be the most probable⁷. ⁸.

Applications for Chelating Agents

The foregoing discussion was presented in order that there be some understanding of the theoretical aspects of complex formation. This should be of value in determining the applicability of chelating agents to specific practical problems.

At the present time, the applications for the aforementioned chelating agents are numerous, and their



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CAMBOSCO SCIENTIFIC COMPANY 3739 ANTWERP ST. • BRIGHTON STATION BOSTON, MASS., U. S. A. number will increase tremendously as these compounds become better known. It must be remembered that they represent recently developed compounds in the field of organic chemistry and their progress will undoubtedly parallel that made in the field of wetting agents. When the latter were first investigated their uses were also limited, but today they have unlimited applications.

However, some uses for chelating agents are definite and tested applications beyond the laboratory stage. The following represent some of the principal ones now in use.

As pointed out numerous times in this discussion, these chelating agents form non-ionic compounds with the alkaline earths and other metallic ions which we know to be the cause of hardness in water. The complexed compounds resulting do not react with soap or other reagents which commonly cause objectionable precipitates with these ions. The chelating agent effectively removes this hardness from water and does so without the formation of precipitates such as are formed with ordinary water softening agents. Therefore, another important advantage in the employment of chelating agents is the fact that filtration of the water so softened is not necessary. In fact, it has been shown that such materials assist in the cleansing and foaming action of the soap and thus serve a multiple purpose. It should be pointed out, however, that these chelating agents are not wetting agents as we know them; neither do they foam appreciably nor have noticeable detergent action.

High temperatures have no effect on the stability of these compounds and their resulting complexes and hence, they may be used at any temperature. Their action is also effective for indefinite lengths of time. Fortunately, complete softening of water is usually not necessary and less chelating agent may be used than required by calculations.

A chelating agent will not only keep metal ions in solution in the presence of precipitating agents for the metal ions, but will also dissolve insoluble metal salts after they have been previously precipitated. A chelating agent, when added to water and used in various types of equipment, will dissolve such common objectionable deposits as calcium sulfate, alkaline earth carbonates, and insoluble phosphates.

The following reactions are typical of this application:

- (1) $CaSO_4 + Na_4Y \rightarrow Na_2(CaY) + Na_2SO_4$.
- (2) $MgCO_3 + Na_4Y \rightarrow Na_2(MgY) + Na_2CO_3$.
- (3) $Ca_3 (PO_4)_2 + 3 Na_4 Y \rightarrow 3 Na_2 (Ca Y) + 2 Na_3 PO_4.$
- (4) $BaSO_4 + Na_4Y \rightarrow Na_2(BaY) + Na_2SO_4$.
- (5) $CaC_2O_4 + Na_4Y \rightarrow Na_2(CaY) + Na_2C_2O_4$.

The commercial chelating agents will dissolve the above precipitates even though such precipitates usually have maximum insolubility in bases.

The chelating agent used in this application has the advantage that the process may be carried out while the equipment is in regular use. Since it acts in both neutral and alkaline solutions, its use avoids the difficulty of bringing metal parts of the processing equipment in contact with the harmful acids which usually

would be used to dissolve such hard objectionable scale deposits.

A chelating agent is a buffering agent and has sufficient reserve alkalinity to saponify fats, grease, oils, etc. Usually a small amount of wetting agent is used in conjunction with the chelating agent.

Conclusion

It is hoped that the facts presented will enable those interested in these chelating agents to find uses for them in their particular operations, but, since conditions vary in each plant, certain deviations from the points outlined may have to be made. The sensible procedure to follow when testing these compounds in some particular application is to initiate investigations on a laboratory or pilot scale. Whether or not the chelating agent will do what is desired is a matter of trial. Just as others have found under the same circumstances, the results may be enlightening.

Acknowledgments

The writer wishes to express thanks to Dr. John J. Singer, Bersworth Chemical Co., Framingham, Mass. for the various data offered by him for use in this article; to Dr. Frederick C. Bersworth of the same company for allowing the writer to use certain information which also appears; to Mr. H. W. Zussman, Alrose Chemical Co., Providence, R. I. for permitting the employment of additional material accumulated by his company. ●

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"Some educators and educated men might claim that education partakes of the character of a fine art, existing for its own sake. Perhaps all of us would accept this point of view to some degree. But most of us would claim that education also has purposes utilitarian, both personal and social. Most statements of the purposes of the college would incorporate the idea that a college education makes a better worker, a better citizen, a person better equipped to meet the varied exigencies of life."

-G. LESTER ANDERSON
University of Buffalo

Writing a Nature Column

(Continued from Page 82)

As editor of the editorial page of the Pittsburgh Sun-Telegraph I found, some ten years ago, that there were frequently little holes on the page that we filled with any miscellaneous material that happened to be available. As I had long been interested in Nature and had accumulated a fund of curious information in regard to our local flora and fauna, I began to write short items on these subjects and to insert them in the editorial page whenever space was available.

The public from the outset showed interest in these items and it was not long until the Nature column became an established feature, published daily on the editorial page for some years and later transferred to the news pages and published on Tuesdays and Thursdays.

I had been interested in Nature from childhood. My father was an amateur botanist and microscopist. When the Carnegie Museum was opened I became a member of the juvenile Andrew Carnegie Naturalists Club and was conducted by Herbert Smith, first curator of the Museum, on field trips. Mr. Smith encouraged me to specialize on Coleoptera and showed me the characteristics of some of the common families of beetles. I had a little biology, particularly botany, at school. And I was always interested in the identification of the birds and fishes and other animals that came under my observation on walks and fishing trips.

It was not, however, until I had the Nature column well under way, and was 60 years of age, that I began anything like a serious study of Nature. Then I took some courses in botanical taxonomy and ecology at the Evening School of the University of Pittsburgh, joined the Botanical Society of Western Pennsylvania and the Audubon Society of Western Pennsylvania, went on field trips, attended lectures, sent specimens to be identified to the Carnegie Museum, the Academy of Natural Sciences at Philadelphia, the Smithsonian Institution at Washington, the Bureau of Entomology at Washington, the biology department of Cornell University, and other institutions, corresponded with many authorities on natural history, accumulated many books on the subject, and read enormously.

The column could almost be maintained at times by the contributions of readers eager to tell of their experiences with and observations of birds and wild flowers in particular, but also snakes, mammals, and occasionally insects. Among insects the praying mantis (Mantis religiosa) is a perennial subject of interest.

At one time I occasionally went far afield in my search for novelties for the column and was as technical as I dared to be, always giving the scientific name as well as the common name to insure accuracy. But the Latin and Greek names used by the taxonomists irritated some of the readers and I seldom use them now. Moreover, as the years have passed, I have found less and less need to go far away for material. I

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confine myself almost exclusively to Western Pennsylvania, and largely to the neighborhood of my home.

With respect to scientific names I find the five years that I devoted to the study of Latin and the four years that I gave to Greek as a youth are paying off handsomely in the help they give me in understanding the meaning of scientific names. I thoroughly agree with Father Patrick J. Holloran, S.J., formerly president of St. Louis University, who in a recent statement on the value of Latin as a high school subject, said: "In the whole field of cultural subjects, Latin will aid us as can few other subjects."

In my own experience it is invaluable in the study of natural history. ●



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—James R. Killian, Jr., Pres., MIT The Obligations and Ideals of an Institute of Technology

Teaching Physics

(Continued from Page 87)

on a percentile scale of the scores made on a standardized test by a group of 204 pupils out of a junior class of 403 members. Forty-two additional members of the same class who had high science aptitude took "college preparatory" physics from another instructor. The scores are "light" at each end, but it shows that only one per cent failed, even though 61 per cent of the class had elected to study physics. As far as test scores show, the less select group of pupils learned more physics than a more select group learned when the conventional technical approach was used.

The writer believes that in our secondary schools, science is for all pupils and not for a selected few. To be understood by all the subject matter must be taught on the interest and ability levels of the group. Those of high science ability cannot be neglected, and therefore must be given an enriched program. This can be met through science clubs, special reports, assignments as assistants in the laboratory, or similar work in which the individual may be interested. •



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Rare Earth Elements

(Continued from Page 92)

which might be abbreviated H_4 enta and which is useful as its sodium salt for water softening, gives acids of the type H[Ln(enta)]CLn = any rare earth element) and salts containing the anion $[Ln(enta)]^-$. These, too, are useful for ion exchange separations. So-called β -diketones,

give what are termed inner complexes. These are species which are non-ionic molecular substances. They are very soluble in solvents such as chloroform or benzene. Similar complexes are formed by 8-quinolinol,

These materials are of analytical interest. Only a few other complexes have been described. It is apparent that in this characteristic, the rare earth metal ions are vastly different from the simple transition metal ions.

Separation of Rare Earth Ions

The separation of these closely related species may be regarded as one of the classic problems of inorganic chemistry. As such it has always constituted the major problem in the field of rare earth chemistry, and for many years it was essentially the only problem. Even now, although much has been done to facilitate separations, it is under continued active investigation.

With the exception of those limited procedures which depend upon oxidation or reduction, all separation procedures are fractional in character. This means that a given step in the approach gives only a generally slight enrichment of the desired component in the initial mixture and must be repeated over and over again. Such approaches are costly, notably inefficient, and often exceptionally time consuming. For materials which occur in small quantities, these techniques are more commonly techniques of concentration rather than separation since they become too inefficient long before pure materials are obtained.

A single blanket separation of the entire series by precipitating with sodium sulfate is commonly utilized as a preliminary step. This divides the materials into the cerium group (atomic numbers roughly 57-64), as difficultly soluble double sulfates, and into the yttrium group (yttrium and atomic numbers 64-71), as more soluble double sulfates. To these concentrates, procedures which may be classified as

- 1. Fractional crystallizations
- 2. Basicity approaches
- 3. Oxidation-reduction methods

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Fractional crystallizations are classic procedures and still those of greatest technical importance. By choice of suitable simple or double salts, alone or in combination, all of the materials may be separated in this fashion, but only separations of the more abundant members are efficient. Basicity approaches depend upon the steadily decreasing basicities of the tripositive ions with increasing atomic number. These differences may involve fractional precipitation of insoluble compounds or complex ion formation. The latter approach has been used most effectively in ion exchange procedures where a mixture of cations is adsorbed on an exchange column and then removed fractionally by means of a complexing agent such as citrate, the heaviest rare earth metal ions coming off first because of the greater stabilities of their complexes. This technique can separate all of the species in exceptionally high states of purity, but it is most useful for small quantities of material. Oxidation-reduction procedures are of course limited to the separation of those few elements which can be oxidized to the +4 state (Cl, Pr, Tb) or reduced to the +2 state (Sm, Eu, Yb). Since in these states of oxidation the elements are entirely different in properties from those in the +3 state, quantitative separations of very pure materials in comparatively few steps are possible. The method has been used most successfully with cerium and europium. Solvent extraction procedures give many promises of providing the ultimate solution to these problems. Recent work on extraction of nitrate solutions, using tributyl phosphate as the non-aqueous solvent, has given separations exceeding in efficiency by many times those obtained by any other fractionation approach. These have the added advantage of continuous operation.

Why Study Rare Earth Chemistry

The above brief summary gives some indication of both the problems involved in this field and the importance of solving them. In brief, the chemistry of these elements is important in providing materials the properties of which will be useful both to the theoretical man and the practical industrial producer. It is one field of inorganic chemistry in which no conceivable limitations for study exist.

Acidity and Basicity

(Continued from Page 89)

light on the processes involved in the ionization of amines and hydrogen acids in water and related solvents, and also on the functioning of acidic and basic catalysts.

The Bureau has found that differentiating reactions with different bases in inert solvents are not peculiar to bromophthalein magenta E but are characteristic of other acidic indicators as well, although the results are not usually so striking. Bromophenol blue resembles bromophthalein magenta E in that it shows differentiations.

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tiating reactions with different classes of organic bases in such solvents, but its behavior is more complex because of its sulfonic acid group.

Although it is clear that acidic indicators cannot be applied in organic liquids in exactly the same way as in water to measure pH values, the NBS studies have shown their value as analytical tools in a variety of applications. To illustrate, a benzene solution of bromophthalein magenta E is useful in distinguishing between aromatic and aliphatic amines as well as between many primary, secondary, and tertiary aliphatic amines. Indirectly, it can be used to test for acidity; for example, a small amount of a tertiary amine turns the solution magenta, but an added acid will combine with part of the tertiary amine and the color will revert toward yellow. Equally important is the application of the indicator to quantitative measurement of the relative strengths of bases in hydrocarbons; such measurements have shown that use of the aqueous ionization constants of bases may lead to false estimates of the reactivity of the bases in hydrocarbons. Other uses include a simple test to determine whether a solid is the salt of an organic base (such as an alkaloid, an aliphatic amine, or a derivative of formamidine or guanidine), detection of bases in chromatography, and location of the endpoint in certain nonaqueous titrations.

Investigations of acidity and basicity in organic solvents are continuing at NBS. In addition to the work with acid indicators, the Bureau is now engaged (Continued on Page 112)

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Acidity and Basicity

(Continued from Page 111)

in studies of the reactions of basic indicators with acids in these solvents. \bullet

RECOMMENDED READING

Further information may be obtained from the following papers:

Acid-base reactions in benzene and other organic solvents: Behavior of bromophthalein magenta with different classes of organic bases, by Marion Maclean Davis and Priscilla J. Schuhmann, J. Research NBS 39, 221 (1947) RP 1825.

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Acid-base equilibrium constants for the reaction of tribenzylamine with picric acid and with trinitro-m-cresol in benzene, from spectrophotometric data, by Marion Maclean Davis and E. Anne McDonald, J. Research NBS 42, 595 (1949) RP 1997.

The dissociation constant of dimethylaniline hydrochloride in chloroform by Marion Maclean Davis, J. Am. Chem. Soc. 71, 3544 (1949).

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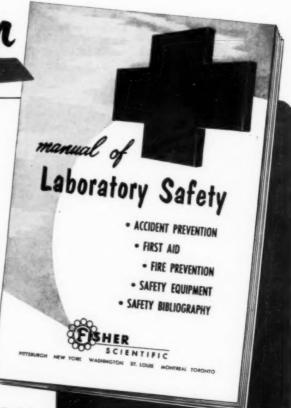
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